THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI FEBRUARY 1951 No. 2

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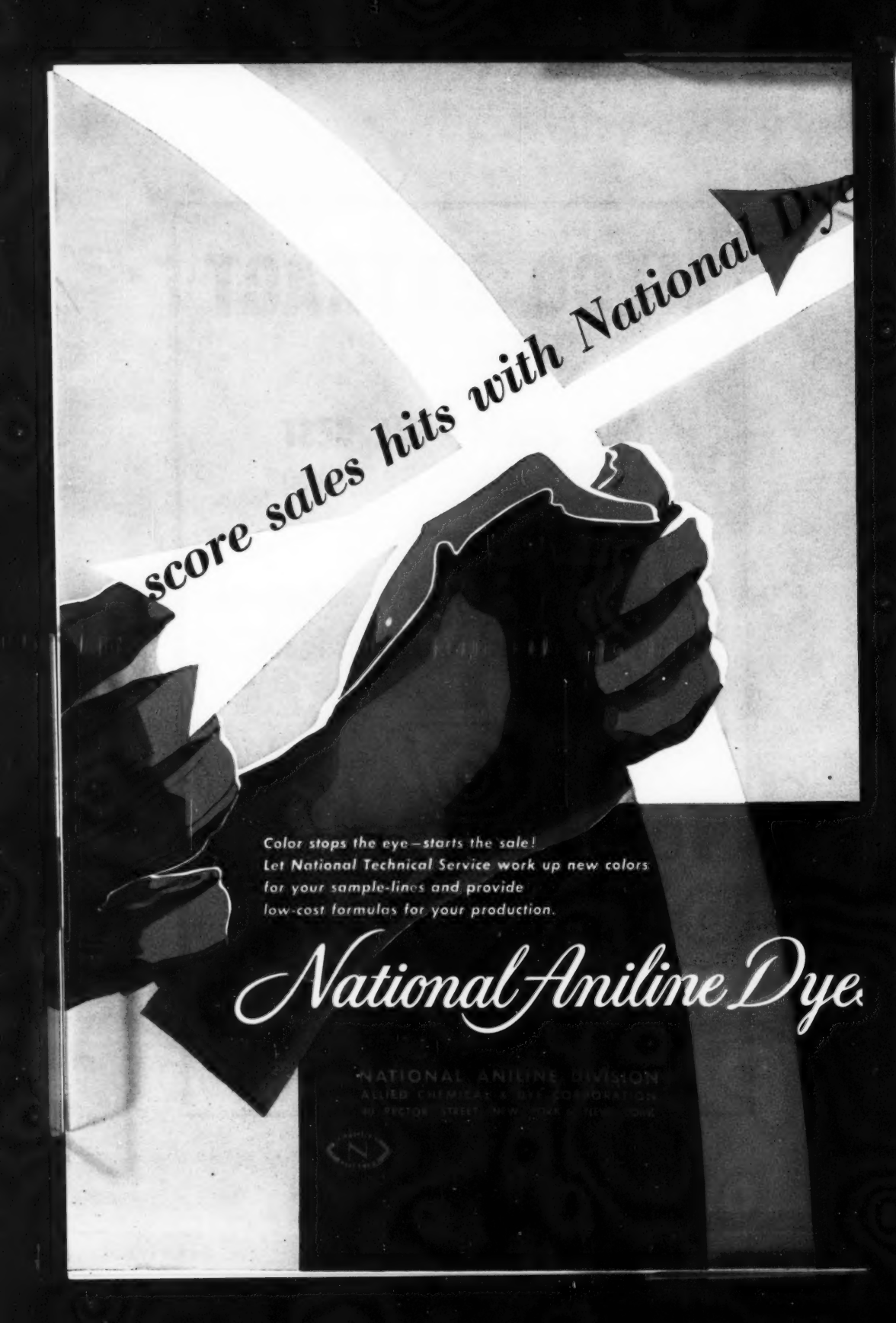
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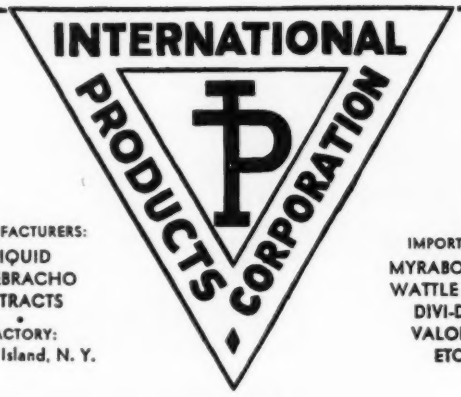

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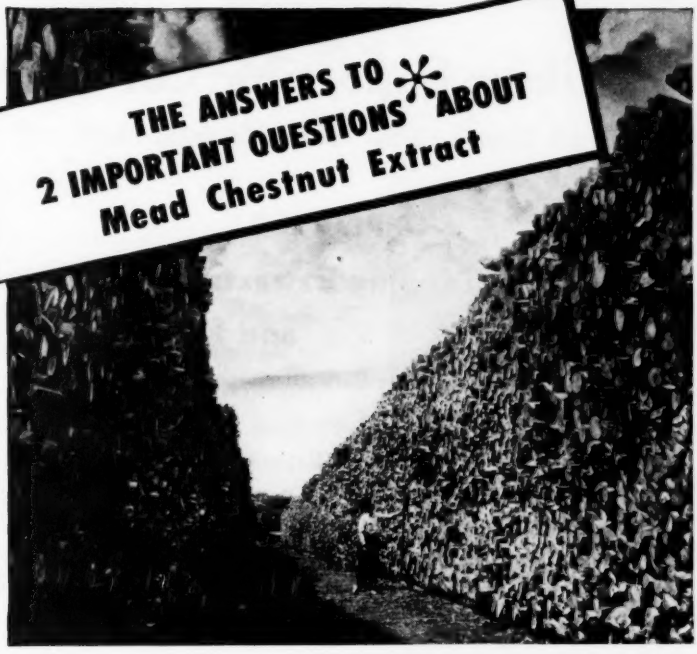

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VOL. XLVI FEBRUARY 1951 No. 2

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SECRETARY'S NOTICE

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The Management Committee of the Dorothy Jordan Lloyd Memorial Fund (British Leather Manufacturers' Research Association) are prepared to award a Travelling Fellowship not exceeding £400 to assist a scientist (junior or senior) to go abroad, or a scientist in the British Commonwealth or the United States to visit this country, to study some aspect of the science and technology of leather manufacture. Applicants wishing to be considered for the 1951 award should send details of their qualifications and of the work they wish to undertake or the project they have in mind, to the Secretary, Dorothy Jordan Lloyd Memorial Fund, B.L.M.R.A., Milton Park, Egham, Surrey.

REPORT OF KAOLIN COMMITTEE

A sample of kaolin furnished by the A. H. Thomas Company, Philadelphia, Pennsylvania and representing a lot designated as Lot No. 2 has been tested by the Tannin Analysis Supervisory Committee. The average values found by the members of this committee as compared with those obtained for official Kaolin Lot No. 1 and the A.L.C.A. standards are as follows:

	Per Cent Moisture	pH	Residue-Water Grams
A.L.C.A. Standards	—	4.5–6.0	Less than .0010
Official Kaolin Lot No 1	0.31	5.87	.0009
Proposed Lot No. 2	0.50	5.82	.0009

The committee has approved Lot No. 2 and has authorized the A. H. Thomas Company to issue the kaolin in this lot as A.L.C.A. Official Kaolin Lot No. 2 which was declared official November 24th, 1950.

G. W. Stanbery, *Chairman.*

JOHN A. POTTS

John A. Potts was born near Pine Grove, Pa., Jan. 9, 1889 and died Sept. 4th, 1950. He was educated in Pine Grove township schools. His first position in the leather business was with G. H. Gensemer in 1906 as a liquor runner. He soon realized that a knowledge of chemistry was of great importance in the production of leather and in order to obtain this knowledge, he took a course in chemistry with the International Correspondence School of Scranton, Pa.

He was superintendent of the Park Run Tannery in Lancaster, Pa., Gensemer & Salem Pine Grove, Pa., Pine Grove Tanning Co. and Virginia Oak Tannery Inc., Luray, Va.

John Potts was well known to many A.L.C.A. members, having joined the Association in 1925, and will be missed at conventions where he was a regular attendant, being very much interested in Association activities.

He was a leader in Pine Grove community activities such as the American Legion, Rotary Club, Masons, and many other groups.

EDWIN SHELLEY CAVETT

In July, the many friends of Edwin Shelley Cavett were sadened to learn of his untimely passing.

Bud, as he was affectionately known to his friends, was born in Denver, Colorado, 6 February, 1899. He was educated at the University of Cincinnati, obtaining his engineering degree, B. Ch. E. in 1923, and the professional degree Ch. E. in 1927.

After leaving Cincinnati, Bud went with the former C. C. Smoot and Sons Company in North Carolina, leaving there in 1924 to become chemical engineer in charge, Tannery Waste Disposal Commission of Pennsylvania, where he remained through 1927. At that time, he joined the A. C. Lawrence Leather Company at Peabody, Massachusetts, as chief chemist of their research division.

In 1933, he became technical director of the tannery division of the Marden-Wild Corporation in Boston, Massachusetts. In September of 1937, be became sales representative of the Mutual Chemical Company of America, which post he held at the time of his passing.

Bud was a member of the American Leather Chemists Association, Institute of Chemical Engineers, and fellow of the Institute of Chemistry.

Bud, in his quiet way, was active in the affairs of the American Leather Chemists Association being interested in both its technical and social events and always willing to lend a helping hand in the days work. His passing will leave a void in our membership.

It might then be written that he was always kind, considerate and helpful, and many of our members are richer in service by reason of his thoughtfulness and kindly interest. We, who have known him intimately will treasure the memory of an able chemist, a patriotic American and a loyal and true friend.

Edwin Raymond Theis.

COUNCIL MEETING MINUTES

A meeting of the Council of the American Leather Chemists Association was held at the Ohio Leather Company, Girard, Ohio on October 24, 1950.

President Koppenhoefer presided. All Officers and Ordinary Members of Council were present. Mr. Dean Williams was a visitor.

The minutes of the meeting held at the close of the Annual Meeting were read and approved. These were published in the October issue of the Journal.

Dr. Turley, Technical Coordinator, reported that some confusion existed in reference to the Physical Testing Subcommittee. Dr. Koppenheofer is to write to Mr. M. Maeser and Mr. J. Harnly and make satisfactory arrangements. Motion was made and seconded and unanimously carried approving that the chairman of a permanent committee be allowed to serve both on permanent and subcommittee, if desired.

The Secretary was instructed to write each committee chairman, and to put a note in the Journal to members, asking them to advise the Secretary of any changes or corrections which it would be desirable to make in the methods. These corrections must reach the Secreatary within sixty days.

Upon motion made, seconded and unanimously carried, it was agreed to discharge the ALCA-FSB Committee when they make their final report to Council. The Secretary is to write them asking for this report. All Future matters concerning KK - L - 311 are to be referred to the new Standards and Specifications Committee, Mr. C. Telander, Chairman. Mr. Telander as chairman of the chemical section of the FSB - ALCA Committee reported progress on the revision of KK - L - 311 and called Council's attention to the matter of a grease determination method. Council considered the matter and also the matter of nitrogen determination was discussed. These matters had already been referred to the committee on Pretannage Processes and are being investigated by Dr. Merrill.

Report of Committees.

Vegetable Leather - No report by G. W. Schultz. Dr. Turley reported that he had some correspondence with Mr. Schultz and advised him that the chairman was to select his subcommittee chairman and the Council would approve his choice.

I. D. Clarke, chairman of the Hide Powder Subcommittee had no report.

The matter of International Union Commissions was briefly discussed.

There are two such commissions:

(1) Hide Powder, which is assigned to our Tannin Analysis Subcommittee.

(2) Leather Analysis, which has not yet been assigned.

A letter from Mr. Standberry was read in which he asked about the proposed methods for determining iron and copper. It was reported that these items were reported to Editor Williams (letter of September 10, 1948) and through some oversight were not published. These will be included in the next issue of the Journal.

French Chrome Hide Powder is a separate subcommittee and has Mr. L. Sheard as chairman. Mr. Sheard reported a plan of work to President

Koppenheofer on January 15, 1950. President Koppenhoefer replied to him through Mr. G. W. Schultz, who is chairman of the Vegetable Leather Committee of which the French Hide Powder is a Subcommittee. The Secretary is to write to Mr. Sheard (copy to Mr. G. W. Schultz) asking him to carry out the work outlined in the letter which he sent to President Koppenhoefer on January 15, 1950.

Council instructed the Secretary to write Mr. Sheard with copy to Mr. G. W. Schultz asking Mr. Sheard if he would take up the matter of producing a quantity of chrome hide powder with the Keystone Tanning and Glue Co. When he has some information and estimates of prices he is asked to advise Council.

The Secretary was asked to give Dr. Turley, Technical Committee Coordinator, a list of all committees, their chairman and status.

The Mineral Tannage Committee had no report. It was suggested that the previous correspondence from Dr. R. M. Lollar be given to Dr. Seligsberger through Dr. Turley. Also the Kubelka factor for chrome is to be suggested as a suitable matter for this committee to look into. Dr. Seligsberger is to be informed that he is to select the members he desires for his committee and Council will approve. Dr. Turley is to write to Dr. Seligsberger about these and other matters.

There was no report from the Physical and Mechanical Property Committee. The Secretary was instructed to write Mr. Maeser and ask him to obtain a statement from Mr. Charles Mann of the Sampling Subcommittee on the program which his committee is planning to work on.

There is still a Physical Testing Subcommittee on Flame Resistance. The report of this subcommittee has been submitted for publication in the Journal. Dr. Lollar reported that he had prepared a description of a method and sent it to Mr. Maeser but had received no reply concerning it. The Secretary is to write Mr. Maeser and inquire about this.

New Analytical Techniques Committee—No report.

Tannery Practice Committee—No report.

The Subcommittee on Stream Pollution submitted a report on the New England Industrial Waste Conference. This report has been mimeographed by the Secretary's Office and copies made available through the Tanners' Council. Editor Williams is to get in touch with Mr. Reuning and prepare a suitable abstract for publication in the Journal.

The report of the Auditing Committee was read, approved and submitted for publication.

A letter from Mr. Lincoln was read and it was ordered published in the Journal, together with the Secretary's letter to Mr. Lincoln.

Dr. Flinn sent in a report on the proposed budget for the 1951 meeting. It was agreed that in the future only one original copy and two copies of the proceedings of the Annual Meeting be ordered, which would reduce the reporting cost.

A letter was read from Dr. Hobbs in reference to his committee on By-Laws. He asked for some suggestions on nominations of candidates for office.

Council made the following recommendations:

(a) That Council appoint a nominating committee and this committee prepare a list of candidates for presentation to the membership.

(b) That any group of fifteen members be permitted to nominate a candidate for office.

The details for these suggestions are to be supplied by the committee now revising the By-Laws.

Upon motion made and seconded and unanimously carried it was ordered that no Council Members succeed themselves in office.

The Business Committee reported that they would make a formal report at the February Meeting.

Dean Williams, the Editor, reported on printing costs and paper. Council asked that 25 copies of the next issue going to press be printed on a cheaper paper and kept separate from the regular Journals, these to be inspected by Council.

The Editor reported that the cost of compiling a 10 year index (1925-1935) would entail one year's time and cost $15,000.00 Council authorized the President to include in his Annual Letter a note regarding this and to enclose return post cards on which interested members could indicate whether they would buy a copy of this index at $10.00 per copy.

Dr. Koppenhoefer reported that Mr. Teas had phoned to him and regretted that he could not attend the Council Meeting.

Council recommended that the Convention Committee announce at the opening meeting of the Annual Convention that all papers presented at the Annual Meeting are the property of the ALCA for publication in the Journal unless released by a written statement from the Editor; that this fact be included in the instructions furnished to persons selected for papers and to all persons whose papers are accepted for presentation at the meeting.

Dr. R. Hobbs was approved by Council as a new member of the Editorial Board to succeed the late Mr. Winheim.

The Resolutions made by the Business Committee were considered and the following recommendation was made to the By-Laws Committee:

Include an article to the effect that the expenditure of money for extraordinary purposes (other than routine expenses) shall be approved by the membership. After a full discussion, Council decided that the decision as to what constituted routine expenses is a matter for Council action since, obviously, small items of expenditure out of the ordinary could not be referred to the membership.

Memorial Resolutions were ordered for the passing of A. H. Winheim and

T. F. Oberlander. These are to be arranged for by the President, then spread on the minutes and copies are to be sent to the widows of the deceased.

ADE H. WINHEIM

At a meeting of the Council of the American Leather Chemists Association held October 24, Nineteen Hundred Fifty, the following Memorial was unanimously adopted:

Whereas, Ade H. Winheim, past President of the American Leather Chemists Association departed this life on the Third Day of June, 1950: and Whereas, his most untimely passing has deprived his industry, his associates and his countless friends of the inspiration of his leadership, and

Whereas, in his passing the American Leather Chemists Association has lost one of its most progressive leaders. Now, therefore, be it

Resolved, That the entire membership of the American Leather Chemists Association, its officers and directors, record large upon the minutes of the Association, our admiration and deep affection for Ade Winheim, and our great sense of loss in his passing.

THEODORE F. OBERLANDER

At a meeting of the Council of the American Leather Chemists Association held October 24, Nineteen Hundred Fifty the following Memorial was unanimously adopted:

Whereas, Theodore F. Oberlander, past President of the American Leather Chemists Association departed this life on the Tenth Day of June, 1950: and Whereas, his untimely passing has deprived the industry of one of its outstanding technicians, and his friends and associates of the benefits of his counsel and advice, and

Whereas, in his passing the American Leather Chemists Association has lost one of its staunch supporters and an acknowledged leader. Now, therefore, be it

Resolved, That the entire membership of the American Leather Chemists Association, its officers and directors, record large upon the minutes of the Association, our admiration and affection for Ted Oberlander, and our great sense of loss in his passing.

And, be it further Resolved, That a copy of this Memorial be delivered to his wife as a sincere expression of our feelings.

Council unanimously ordered a Winheim Memorial Award to be given every other year for the next ten years. Dr. Windus is to prepare the details of the award.

ADE WINHEIM MEMORIAL AWARD

The American Leather Chemists Association desires to honor the memory of Mr. Ade Winheim for his tireless and devoted efforts in behalf of the progress of the Association.

To this end the Ade Winheim Memorial Award is hereby established. This award shall consist of a cash prize of one hundred dollars from the funds of the Association. It will be granted to a student for the presentation of a meritorious paper. The award will be determined by the ALCA Awards Committee. The prize will be given biennially for a period of ten years.

Mr. Robert Cushing, one of the original members, was made a Life Member. The Secretary is to so advise him.

The resignation of Mr. John L. Wilson was accepted.

It was agreed that Dr. Koppenhoefer would answer the Dorothy Jordon-Lloyd Memorial correspondence. The vote by members was 58 Yes, 102 No.

Twenty-eight members were ordered dropped for non-payment of dues.

There being no further business, upon motion duly made, the meeting was adjourned.

FRED O'FLAHERTY, *Secretary.*

Studies in Two-Bath Chrome Tanning

I. The Influence of the Reduction Bath on the Fixation and Distribution of Chromic Oxide and Sulfur in Leather.

KARL KLANFER and PAUL KENEDI

Chemical Laboratory of the S. A. Cortume Carioca, Rio de Janeiro, Brazil

While the one-bath chrome tanning process has been the subject of very intensive studies, the two-bath process has been investigated rather inadequately. The reason for this is the much greater commercial importance of the one-bath process. However, the two-bath process is still used for the manufacturing of certain types of leather, especially for glazed kid, some technical and mechanical leather, and sometimes also for the tanning of horsehides and sheepskins; therefore, studies of the two-bath process should be of interest. In recent times, the two-bath process has been studied by Stiasny and Papayannis [1] and by Theis and Kalb [2].

Our present contribution concerns mainly the mechanism of the second bath. The method of layerwise analysis of the leather was used in these investigations. This method, which Kritzinger and Theis [3] call stratographic analysis, has been successfully used for the study of the one-bath chrome

*Presented at the Forty-Fifth Annual Meeting of the American Leather Chemists Association, The Monmouth Hotel, Spring Lake, June 24, 1949.

tanning by several authors, especially by Schindler and Klanfer [4] by Theis and Weidner [5] and by Kritzinger and Theis [3].

A. Experimental

Brazilian goatskins were soaked, limed and bated. An overnight bate was used and the skins were almost completely delimed. From these bated skins, heads, bellies and shanks were cut off and the remainder was cut into squares, weighing 10 grams each and about 9 square inches (3 x 3 inches) in area. For each series of experiments a rather large number of these skin squares was used (about 60 to 80).

These bated skin squares were thoroughly washed and, unless stated to the contrary, received a pickle (in a glass drum) consisting of 100 per cent water, 6 per cent salt and 2 per cent hydrochloric acid for 2 hours. The percentage weights for the pickle and for the first and second bath were calculated on the weight of the bated skins. After pickling the skins were transferred to the first bath consisting of 200 per cent water, 5 per cent sodium bichromate and 2.5 per cent hydrochloric acid (*). In this first bath the skins ran for 6 hours and were left overnight in the bath. The next day the skin pieces were taken out and piled up for 24 hours.

These skin pieces, *which all had the same first bath*, were now placed in the reduction bath. This reduction bath was made up with 300 per cent water, 15 per cent hypo and varying amounts of hydrochloric acid. The hydrochloric acid was added in 4 equal feeds, each 15 minutes apart. The skins ran for 6 hours in the reduction bath and were left overnight in the bath. The following day, the skin pieces ran for 2 hours and were then taken out, piled up for 24 hours, then washed in running water for 2 hours, then dyed *without shaving*, fatliquored and dried. The leather pieces were then split into 5 layers, the splitting being done as described by Schindler and Klanfer [4].

An analysis was carried out on the unsplit leather as well as on each layer for nitrogen, chromic oxide and sulfur. Nitrogen was determined by the Kjeldahl method, chromic oxide by the fusion method and sulfur by the method of A. Castiglione [6].

B. First Series of Experiments

The first series of experiments was carried out along the lines previously described, varying the amounts of hydrochloric acid in the second bath between limits of 3 - 8 per cent.

a—Changes of pH During the Reduction

Table I and Figure 1 show the changes in the pH values in the reduction bath. Following the addition of acid, the pH is lowered, but during the reduction, acid is used up and the pH increases. We call the pH at the end of the

*Hydrochloric acid refers to the solution containing 33 per cent HCl
Sodium bichromate refers to $Na_2Cr_2O_7.2H_2O$, hypo means $Na_2S_2O_3.5H_2O$.

TABLE I

Changes of pH in the Reduction Bath
(First series of experiments)

TIME	pH						
	3% HCl	4% HCl	5% HCl	6% HCl	7% HCl	8% HCl	5% HCl 3% Formate
1st addition 15 min.	5.76	5.51	5.47	5.60	5.51	5.39	5.74
2nd addition 30 min.	5.76	5.60	5.40	5.23	4.94	4.24	5.62
3rd addition 45 min.	5.55	5.06	4.19	3.61	3.25	2.80	5.00
4th addition 1 Hour	4.57	3.34	2.86	2.51	2.40	2.00	4.22
1 hour, 15 min.	4.84	3.64	3.22	2.74	2.50	2.12	4.26
1 hour, 30 min.	4.96	3.84	3.33	2.92	2.69	2.16	4.30
2 hours, 30 min.	5.48	4.40	3.78	3.12	2.79	2.28	4.34
3 hours, 30 min.	5.74	4.52	3.89	3.18	2.79	2.32	4.35
4 hours	5.74	4.57	3.90	3.17	2.81	2.32	4.36
22 hours	6.24	4.71	3.98	3.20	2.78	2.33	4.40

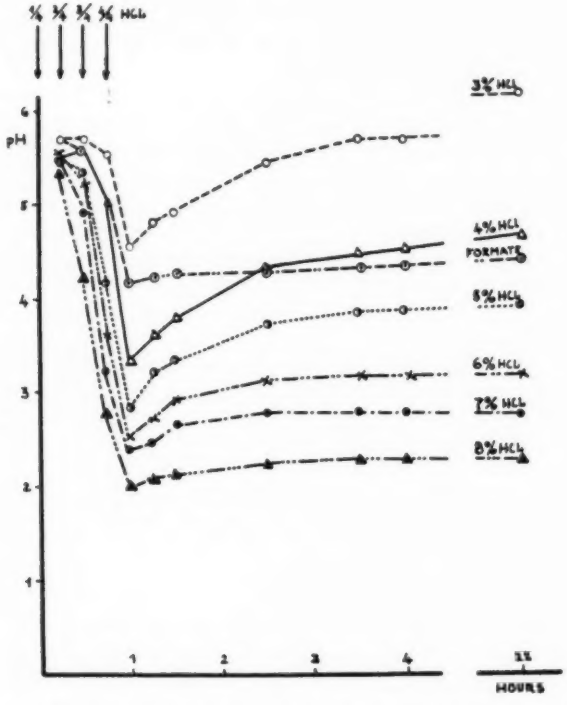

FIGURE 1.—Changes of the pH in the reduction bath. (First series of experiments.)

reduction, on the following day when the skins were taken out, the end pH. For instance when we used 4 per cent hydrochloric acid, the pH fell after the addition of the acid to pH 3.34, but afterwards increased to an end pH of 4.71. The diagram is somewhat simplified. Actually after each addition of acid the pH is lowered rapidly and increases afterwards. With the next addition of acid the pH is lowered further and so on. Our diagram shows only the pH values immediately before the next addition of acid occurs; therefore it shows only one lowest point of pH instead of showing four successively lower points.

TABLE II

Effect of the pH of the Reduction Bath on the Stratographic Distribution of Chromic Oxide.

(First series of experiments)

Reduction at		Per Cent Chromic Oxide						
% HCl	End pH	Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
3	6.24	6.30	7.15	5.10	3.90	6.57	9.70	3.25
4	4.71	5.69	6.40	5.04	4.46	5.80	7.48	1.94
5	3.98	4.70	5.18	4.40	3.95	4.95	6.04	1.23
6	3.20	4.14	4.79	3.74	3.72	4.21	4.96	1.07
7	2.78	3.66	3.90	3.00	2.82	3.36	4.22	1.08
8	2.33	3.20	3.50	2.52	2.37	3.10	3.95	1.13
		With 3 Per Cent Sodium Formate Added						
5	4.43	4.06	4.06	3.60	3.51	3.99	4.83	0.55

b—Stratographic Analysis of the Leather.

1—Chromic Oxide Content

Table II and Figures 2, 3 and 4 give the results obtained by the analysis of the leather. The leathers were split into five layers (grain, grain middle, middle, flesh middle and flesh) and an analysis of each layer was carried out; further, the unsplit leather was analyzed.

First we shall consider the chromic oxide values of the unsplit leather. Table II and Figure 2 show the chromic oxide values of leathers obtained with different amounts of hydrochloric acid in the second bath. We see that with increasing amounts of hydrochloric acid the chromic oxide decreases. For instance when we used 4 per cent hydrochloric acid the leather contained 5.70 per cent chromic oxide calculated on the hide substance. When 7 per cent hydrochloric acid was used, however, the corresponding chromic oxide figure was 3.60 per cent on the hide substance. We can also plot the results against the end pH of the second

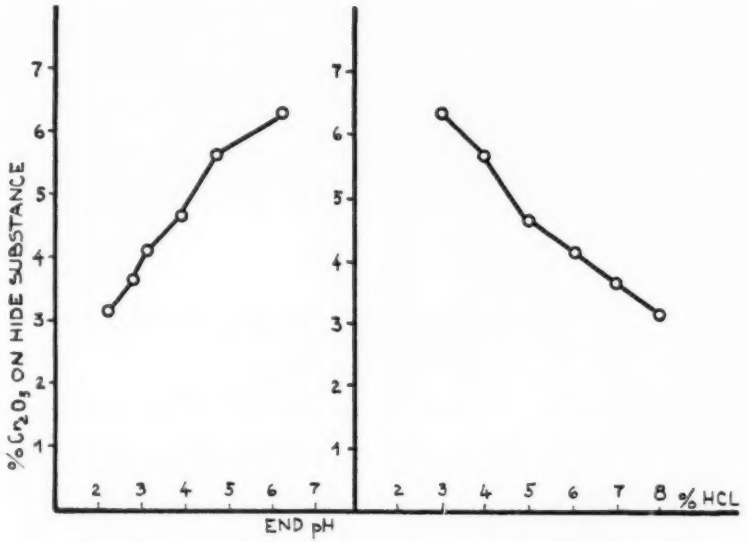

FIGURE 2.—Influence of the end pH and the amount of hydrochloric acid in the reduction bath on the chromic oxide fixation. (First series of experiments).

bath, and note that with increasing end pH leathers with increasing chromic oxide content result.

Table II and Figure 3 show the results obtained by the stratographic analysis. These figures and curves are interesting since they show the actual part played by the acidity of the second bath on the vertical distribution of chromic oxide. At the bottom of Figure 3 we have the curve at pH 2.33 and above this the curve at pH 2.78, while on top is the curve at pH 6.24 showing the highest content of chromic oxide. We note further that the grain and the flesh layers in all cases contain more chromic oxide than the middle and other layers. The leathers coming from a second bath with a low pH give flatter curves, i. e. the grain does not contain much more chromic oxide than the middle and the distribution of chromic oxide is more uniform. On the other hand, leather reduced at a higher pH shows greater differences between the chromic oxide content of grain and middle, i. e., the vertical distribution of chromic oxide is not uniform.

The significance of these results is shown to better advantage in Figure 4, which shows the difference between the chromic oxide content of grain and middle layers against the end pH. We note that up to pH 4 there is

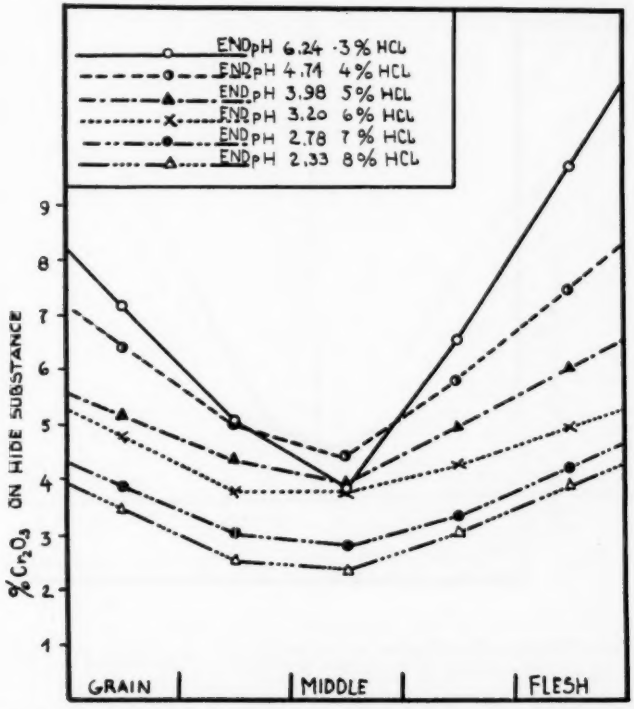

FIGURE 3.—Effect of the end pH of the reduction bath on the stratographic distribution of chromic oxide. (First series of experiments).

TABLE III

Effect of the pH of the Reduction Bath on the Stratographic Distribution of Sulfur.

(First series of experiments)

Reduction at % HCL	End pH	Per Cent Sulfur						
		Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
3	6.24	0.48	0.38	0.32	0.29	0.30	0.68	0.09
4	4.71	0.67	0.69	0.62	0.40	0.44	0.80	0.29
5	3.98	0.87	0.81	0.71	0.41	0.50	0.90	0.40
6	3.20	0.97	1.13	0.82	0.45	0.58	1.02	0.68
7	2.78	1.13	1.34	0.84	0.50	0.63	1.03	0.84
8	2.33	1.14	1.44	0.86	0.53	0.68	1.20	0.91
		With 3 Per Cent Sodium Formate Added						
5	4.43	0.39	0.39	0.30	0.27	0.32	0.55	0.12

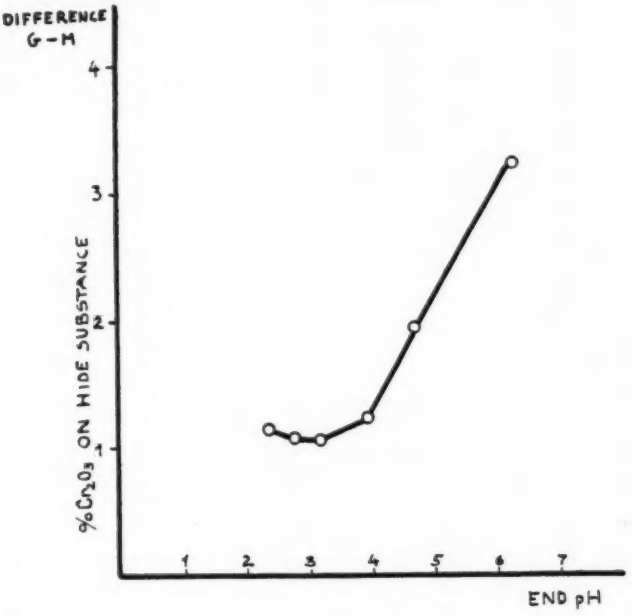

FIGURE 4.—Effect of the end pH of the reduction bath on the difference between the chromic oxide content of grain and middle. (First series of experiments).

little change. Above pH 4 this difference increases rapidly; small changes of pH bring about big changes in the vertical distribution of chromic oxide.

2—Sulfur Content

Table III, Figures 5, 6 and 7 show the results of the sulfur determination. Figure 5 shows the sulfur content of the unsplit leather at different acidities of the second bath. At a high end pH the sulfur content is small and at low pH values the sulfur content is high. *This effect is just the opposite of the effect of pH on chromic oxide.* A low pH in the second bath results in leathers having the maximal values of sulfur and the minimal values of chromic oxide. A high pH in the second bath produces leathers with a high chromic oxide content and a low content of sulfur.

The sulfur was also determined in the leather split into five layers. Table III and the stratogram in Figure 6 show that the effect of the pH on the sulfur distribution is the reverse of the effect on the chromic oxide distribution. The curve with the end pH 6.24 at the bottom of the figure is rather even. The curve with the end pH 4.74 is the next higher one,

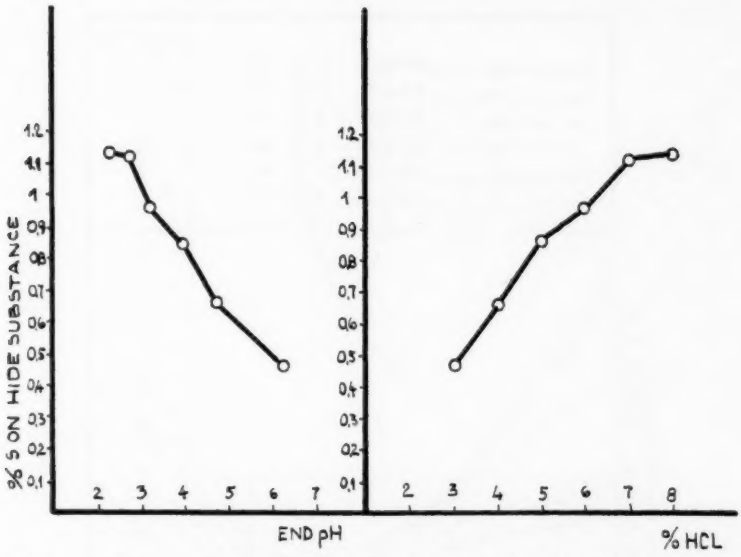

FIGURE 5.—Effect of the end pH and the amount of hydrochloric acid in the reduction bath on the sulfur fixation. (First series of experiments).

and is less even. At the top are the curves with the end pH of 2.33 and 2.78 and both curves are very uneven. If the reduction is carried out at a low pH big differences in the sulfur content of grain and middle result; while if the reduction is carried out at a higher pH small differences between the sulfur content of grain and middle result. Or we can say that:

at a high pH.....even distribution of sulfur
uneven distribution of chromic oxide
at a low pH.....even distribution of chromic oxide
uneven distribution of sulfur

These relations can be shown in the difference diagram in Figure 7. We see that the difference between the sulfur content of the grain and the sulfur content of the middle is large at a low pH and small at a high pH, which is the reverse of the effect noted for chromic oxide.

c—Shrink Temperatures

As could be expected the pH of the second bath has a marked influence on the shrink temperature. Figure 8 shows the shrink temperature after completion of tanning at different end pH levels, and it is noted that the shrink temperature increases with increasing pH up to pH 5 while above an end pH of 5 the shrink temperature is lowered.

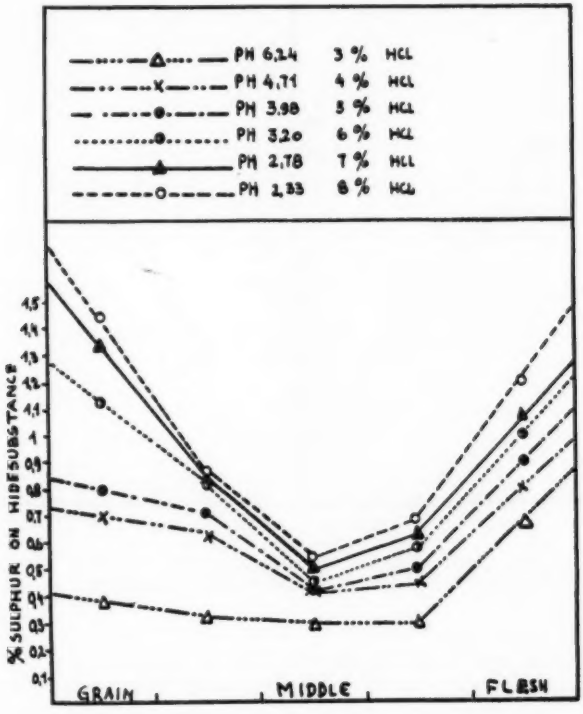

FIGURE 6.—Effect of the end pH of the reduction bath on the stratographic distribution of sulfur. (First series of experiments).

d—Effect of Masking Agents

We know, especially from the work of Theis and Kritzinger[8] and of E. Stiasny[7], that complex forming agents added to the chrome solution of the one-bath tanning process tend very strongly to even out the vertical distribution of chromic oxide in the leather. Stiasny and Papayannis[1] observed a similar effect by using formic acid in the first bath of two bath tanning. We find that the addition of masking agents to the second bath in the two-bath tanning, results in a very uniform vertical distribution of chromic oxide and sulfur in the leather.

For this experiment we used the same procedure as in the previously described experiment. Skin pieces, which were pickled and received the first bath together with the skin pieces from the first series of experiments, were tanned in a reduction bath containing 15 per cent hypo and 5 per cent hydro-

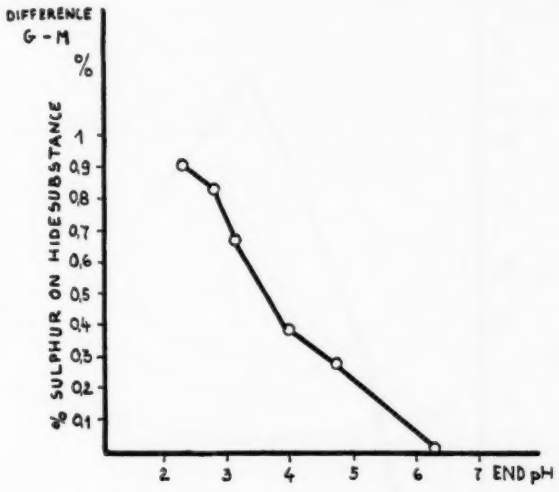

FIGURE 7.—Effect of the end pH of the reduction bath on the difference between the sulfur content of grain and middle. (First series of experiments).

chloric acid; 3 per cent sodium formate was added to the hypo solution before adding the acid.

Table I and Figure 1 show that the pH curve of the formate addition is higher than the corresponding curve with 5 per cent of hydrochloric acid. The pH curve of the second bath with 5 per cent hydrochloric acid shows an end pH of 3.98 while the curve with 5 per cent hydrochloric acid and 3 per cent added sodium formate has an end pH of 4.43. Although the curve of the formate addition shows higher pH values, it has a similar course as the curves with the lowest pH and is actually parallel to the curve with 8 per cent hydrochloric acid without formate.

An analysis was carried out on this leather after splitting into 5 layers. Table II and Figure 9 show the stratographic distribution of chromic oxide in the leather from the reduction bath to which 3 per cent sodium formate was added. For comparison Figure 9 includes the stratogram of the leather from a reduction bath with the same amount (5 per cent) of hydrochloric acid (end pH 3.98) and the stratogram of the leather with 4 per cent hydrochloric acid (end pH 4.71). We see that the curve representing the sodium formate addition is at the bottom of the diagram and is the most even curve. According to the end pH this curve should be between the pH 3.98 and the pH 4.71 curve, but because of the effect of the complex forming sodium formate the curve shows the lowest amount of chromic oxide and the smallest differences between the chromic oxide content of grain and middle. Thus,

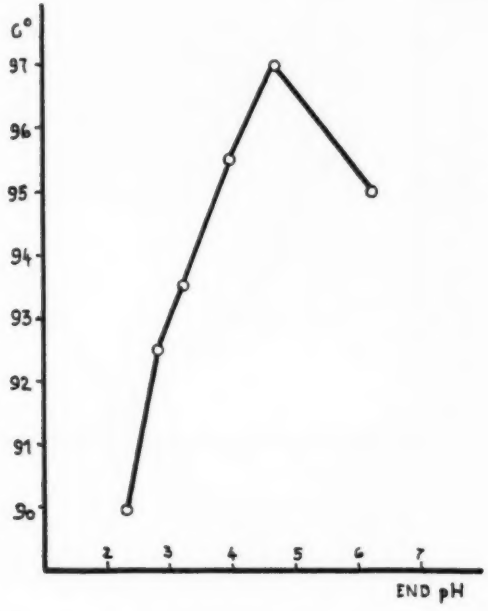

FIGURE 8.—Influence of the end pH of the reduction bath on the shrink temperature. (First series of experiments).

the addition of sodium formate to the second bath brings about a more uniform vertical distribution of the chromic oxide, but the total amount of chromic oxide in the leather is smaller.

It is interesting that the addition of sodium formate has a similar effect on the distribution of sulfur. Table III and Figure 10 show the sulfur distribution in leather from a reduction bath with an addition of 3 per cent sodium formate. The curve at the bottom of Figure 10 shows the sulfur distribution in the leather with the added sodium formate. As in Figure 9, we also give the stratogram of the leather with the same amount of hydrochloric acid (5 per cent), and the curve with 4 per cent hydrochloric acid in the reduction bath. The curve from the leather with the sodium formate addition to the reduction bath shows the lowest values of the sulfur and a much more even distribution than the two other curves. The addition of sodium formate to the second bath has a similar effect on the sulfur distribution as on the chromic oxide distribution. The total amount of sulfur in the leather is smaller but the vertical distribution of sulfur is more uniform.

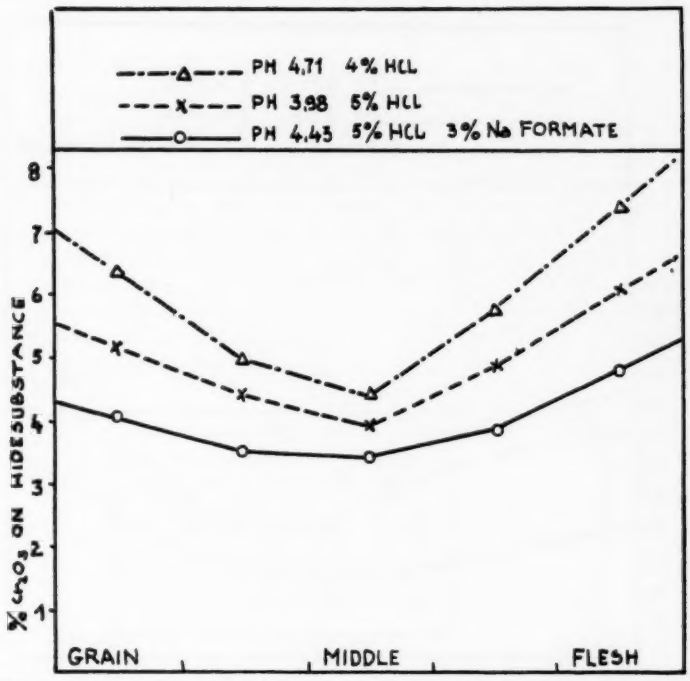

FIGURE 9.—Influence of the addition of 3 per cent sodium formate to the reduction bath on the stratographic distribution of chromic oxide. (First series of experiments).

TABLE IV

Changes of the pH in the Reduction Bath.

(Second series of experiments. Pre-reduction before the reduction bath)

	pH								
Time	1 Per Cent HCl	2 Per Cent HCl	3 Per Cent HCl	4 Per Cent HCl	5 Per Cent HCl	6 Per Cent HCl	7 Per Cent HCl	8 Per Cent HCl	5 Per Cent HCl 3 Per Cent Na Formate
1st addition 15 min.	5.61	5.54	5.54	5.52	5.45	5.32	5.18	5.14	5.46
2nd addition 30 min.	5.26	5.28	5.22	5.12	4.85	4.04	3.96	3.32	5.20
3rd addition 45 min.	5.20	5.13	4.64	3.91	3.07	2.69	2.64	2.38	4.24
4th addition 1 hour	4.90	4.60	3.50	3.06	2.56	2.19	2.11	1.82	3.64
2 hours	4.50	4.60	3.84	3.36	2.84	2.34	2.30	1.97	3.76
3 hours, 30 min.	4.42	4.75	4.17	3.68	3.01	2.48	2.40	2.01	3.77
4 hours 30 min.	4.65	4.78	4.40	3.81	3.06	2.52	2.40	2.1	3.78
5 hours 30 min.	4.79	4.82	4.55	3.83	3.08	2.54	2.40	2.15	3.79
6 hours 30 min.	4.90	5.03	4.58	3.90	3.10	2.63	2.40	2.15	3.80
22 hours	5.58	5.30	4.80	3.92	3.22	2.67	2.55	2.13	3.83

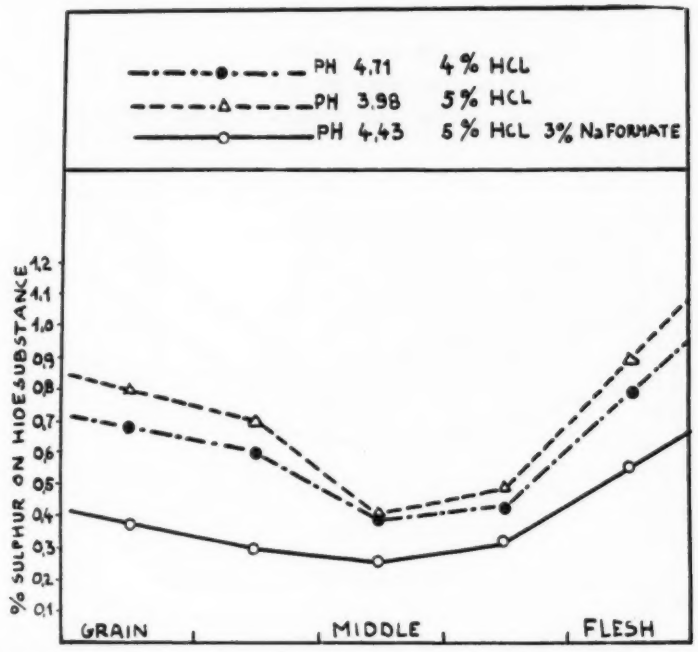

FIGURE 10.—Influence of the addition of 3 per cent sodium formate to the reduction bath on the stratographic distribution of sulfur. (First series of experiments).

TABLE V

Effect of the pH of the Reduction Bath on the Stratographic Distribution of Chromic Oxide.

(Second series of experiments. Pre reduction before the reduction bath)

Reduction at Per Cent HCl	End pH	Per Cent Chromic Oxide						
		Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
1	5.58	5.50	6.05	4.10	3.50	4.40	8.20	2.55
2	5.30	5.35	6.47	4.56	4.30	4.80	7.50	2.17
3	4.80	5.00	5.65	5.00	4.50	4.96	6.70	1.15
4	3.92	4.60	5.27	4.36	4.27	4.77	5.44	1.00
5	3.22	4.20	4.48	3.66	3.40	3.90	4.70	1.08
6	2.67	3.54	3.90	3.15	2.90	3.43	4.10	1.00
7	2.55	3.27	3.86	3.10	2.83	3.40	4.08	1.03
8	2.13	3.00	3.42	2.56	2.44	2.80	3.44	0.98
		With 3 Per Cent Sodium Formate Added						
5	3.83	3.82	3.89	3.70	3.50	3.50	4.40	0.39

C. Second Series of Experiments

In practice a so-called pre-reduction is often applied before the second bath. After the first bath, the skins are usually set out and then dipped in a solution of hypo and acid. The skins are then piled up, and after several hours put into the second bath. We carried out a series of experiments to study the effect of this pre-reduction on the distribution of chromic oxide and sulfur. The procedure used in these experiments was similar to that used in the former series of experiments, except that after the first bath the skin pieces were slightly set out and dipped in a solution consisting of 100 parts water, 7.5 parts hypo and 4 parts hydrochloric acid. After dipping the skins were piled up and on the next day separate lots were put in a series of second baths with 15 per cent hypo and varying amounts of hydrochloric acid. Table IV records the changes in the pH during the second bath.

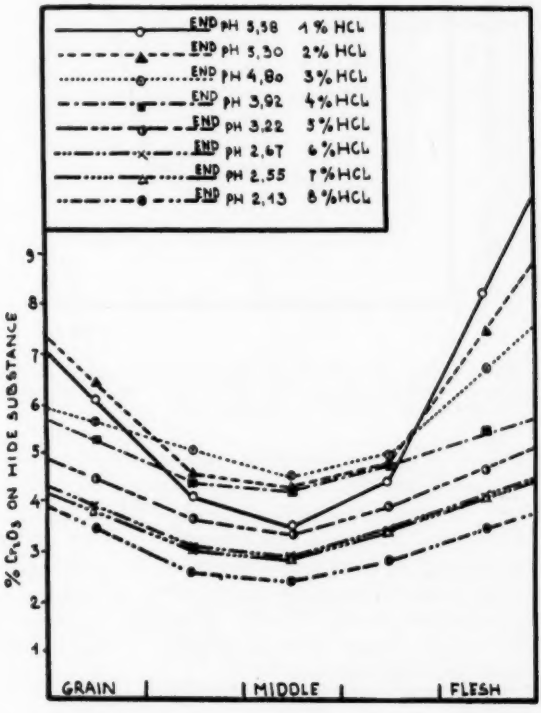

FIGURE 11.—Effect of the end pH of the reduction bath on the stratographic distribution of chromic oxide. (Second series of experiments. Pre-reduction before the reduction bath).

Stratographic Analysis of the Leather

1. Chromic Oxide Content

Table V and Figure 11 show the chromic oxide values of the resulting leathers which were split into five layers. This stratogram shows a rather similar picture to the stratogram of the former series of experiments. Low end pH values give smaller chromic oxide values and a more even distribution of the chromic oxide throughout the leather. At a higher end pH we have again higher chromic oxide values and an uneven distribution.

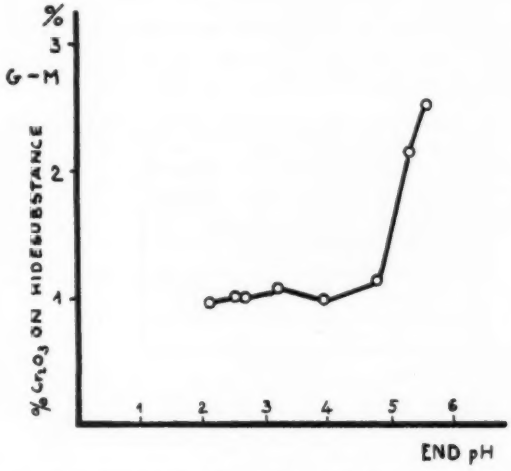

FIGURE 12.—Effect of the end pH of the reduction bath on the difference between chromic oxide content of grain and middle. (Second series of experiments. Pre-reduction before the reduction bath).

Figure 12 dows the curve of the differences between the chromic oxide content of the grain and the middle plotted against the end pH of the reduction bath. Over a comparatively large part of the curve, from pH 2 – pH 4.8, there is no increase in this difference; however, at higher pH values, above about pH 5, a rapid increase occurs. The difference diagram from the former series of experiments (Figure 4) without pre-reduction showed a rapid increase of this difference above pH 4. It seems that the pre-reduction makes a more even distribution of the chromic oxide possible over a larger pH range.

2. Sulfur Content

Table VI and Figure 13 show the stratographic distribution of sulfur in the pre-reduced leather. As in the sulfur stratogram from the first

TABLE VI

Effect of the pH on the Stratographic Distribution of Sulfur

(Second series of experiments. Pre-reduction before the reduction bath)

Reduction at Per Cent HCl	End pH	Per Cent Sulfur						
		Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
1	5.58	0.25	0.11	0.05	0.01	0.05	0.84	0.10
2	5.30	0.68	0.53	0.26	0.13	0.27	1.50	0.40
3	4.80	0.96	0.78	0.39	0.36	0.36	1.70	0.42
4	3.92	1.39	1.14	0.59	0.62	0.79	2.24	0.52
5	3.22	2.10	1.55	0.91	0.74	1.18	2.80	0.81
7	2.55	2.08	1.98	0.90	0.88	1.3	3.10	1.10
8	2.13	2.50	2.16	0.86	0.73	1.2	3.20	1.43
		With 3 Per Cent Sodium Formate Added						
5	3.83	0.68	0.46	0.19	0.0	0.50	1.42	0.46

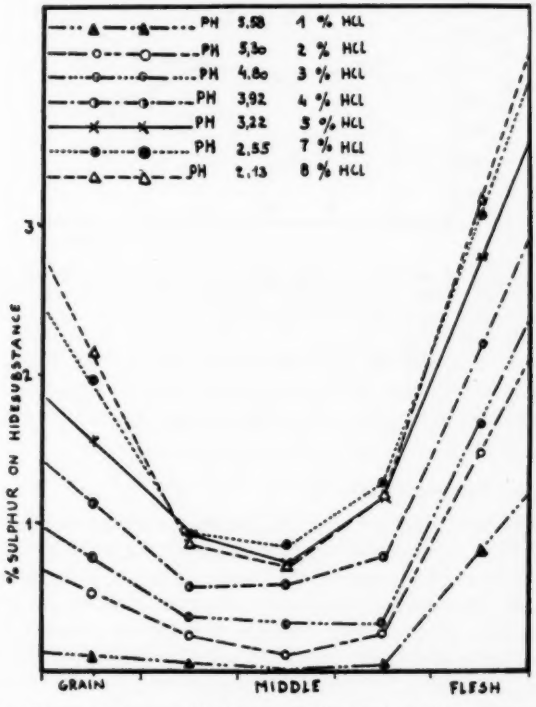

FIGURE 13.—Effect of the end pH of the reduction bath on the stratographic distribution of sulfur. (Second series of experiments. Pre-reduction before the reduction bath).

series of experiments, at low pH levels an uneven distribution and greater amounts of sulfur result, while at a high pH, an even distribution and smaller amounts of sulfur result. The total amount of sulfur is somewhat higher in the pre-reduced leather than in the leather which did not receive a pre-reduction.

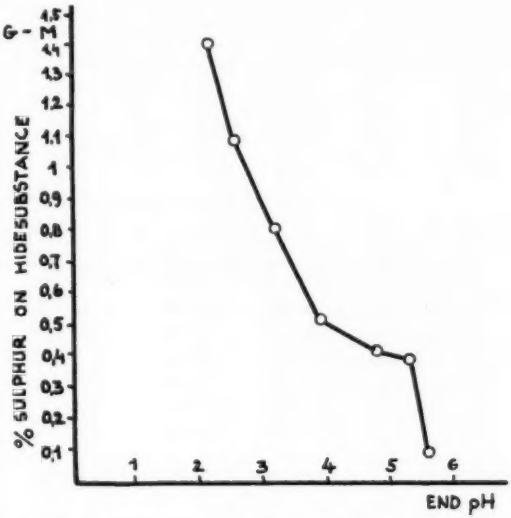

FIGURE 14.—Effect of the end pH of the reduction bath on the difference between the sulfur content of grain and middle. (Second series of experiments. Prereduction before the reduction bath).

Figure 14, which shows the differences between the sulfur content of the grain and the sulfur content of the middle plotted against pH, gives a similar picture to the curve of the leather which has not been pre-reduced (Figure 7).

3. Effect of Masking Agents

The addition of 3 per cent sodium formate to the reduction bath also resulted in the case of pre-reduced leather in a more uniform distribution of the chromic oxide. Further, the total amount of chromic oxide was also smaller. Also, the distribution of sulfur is evened out, and the total amount of sulfur in the leather is smaller through the presence of sodium formate in the second bath. Figure 15 and Figure 16 show this effect of the addition of sodium formate to the second bath on the vertical distribution of chromic oxide and sulfur in the leather. The curve with 3 per cent sodium formate and 5 per cent hydrochloric acid has in this series of

experiments an end pH of 3.83. For comparison the curves without formate with 4 per cent hydrochloric (end pH 3.92) and with 5 per cent hydrochloric acid (end pH 3.22) are added. In both diagrams the curve from the addition of sodium formate to the second bath is at the bottom and is the flattest curve.

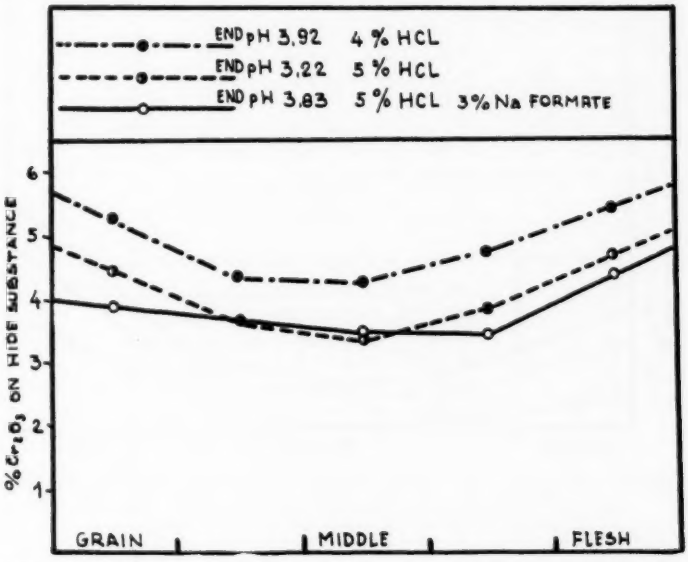

FIGURE 15.—Influence of the addition of 3 per cent sodium formate to the reduction bath on the stratographic distribution of chromic oxide. (Second series of experiments. Pre-reduction before the reduction bath).

TABLE VII

Changes of the pH in the Reduction Bath

(Third series of experiments, without a pickle)

	pH						
TIME	1.5 Per Cent HCl	4.0 Per Cent HCl	5.5 Per Cent HCl	7.0 Per Cent HCl	8.5 Per Cent HCl	10.0 Per Cent HCl	7 Per Cent HCl 3 Per Cent Na Formate
1st addition 15 min.	5.80	5.70	5.62	5.48	5.36	5.32	5.54
2nd addition 30 min.	5.80	5.68	5.54	5.40	5.20	5.00	5.42
3rd addition 45 min.	5.80	5.52	5.20	4.73	3.62	3.04	4.92
4th addition 1 hour	5.78	4.90	3.49	2.44	1.98	1.68	3.72
1 hour, 30 min.	5.92	5.16	4.12	2.99	2.30	1.92	4.00
2 hours	6.24	5.60	4.78	3.69	2.58	2.00	4.08
3 hours	6.48	6.14	5.16	3.70	2.60	2.02	4.08
4 hours	6.60	6.18	5.22	3.78	2.66	2.08	4.10
22 hours	7.28	6.28	4.84	3.70	2.66	2.12	4.14

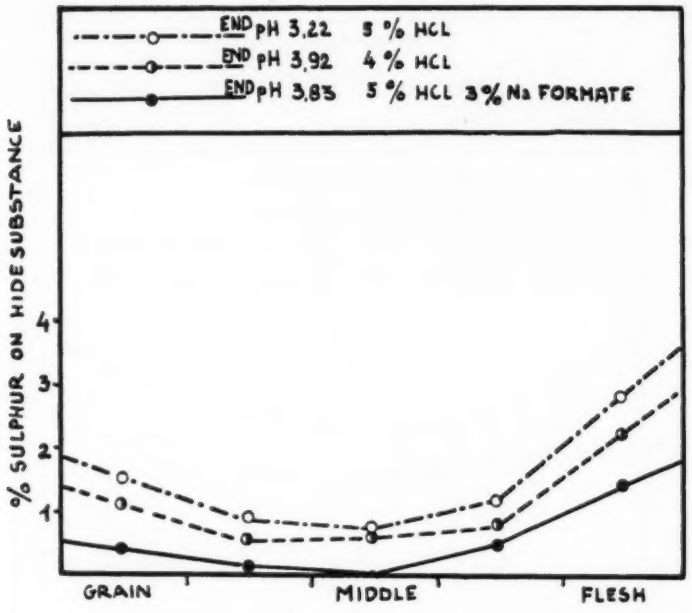

FIGURE 16.—Influence of the addition of 3 per cent sodium formate to the reduction bath on the stratographic distribution of sulfur. (Second series of experiments. Pre-reduction before the reduction bath).

D. Third Series of Experiments

The experiments described so far were all carried out with a pickle before the first bath. In the practice of two-bath tanning this pickle is often omitted and the skins come directly after bating and washing into the first bath. To approximate this practice we repeated the first series of experiments leaving out the pickle. Table VII shows the changes of the pH during the reduction of the unpickled leather and we note that by leaving out the pickle we reach higher pH values.

Stratographic Analysis of the Leather

1. Chromic Oxide Content

Table VIII and Figures 17 and 18 give the results of the leather analysis and show the effect of the pH of the second bath on the chromic distribution.

The stratogram in Figure 17 shows that the unpickled leather has a higher chromic oxide content than the pickled leathers with the same

TABLE VIII

Effect of pH on the Stratographic Distribution of Chromic Oxide
(Third series of experiments, without a pickle)

Reduction at Per Cent HCl	End pH	Per Cent Chromic Oxide on Hide Substance						
		Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
1.5	7.28	5.20	5.56	3.58	2.70	4.20	9.65	2.86
4.0	6.28	7.25	6.90	4.10	3.80	6.14	10.60	3.10
5.5	4.84	6.78	7.98	5.68	5.60	7.10	8.45	2.38
7.0	3.70	5.13	6.55	4.70	4.80	5.30	7.00	1.75
8.5	2.66	3.50	3.94	2.90	2.93	3.68	5.40	1.01
10.0	2.12	3.22	3.50	2.39	2.40	3.26	4.95	1.10
		With 3 Per Cent Sodium Formate Added						
7	4.14	4.30	4.79	3.88	4.00	4.36	5.94	0.79

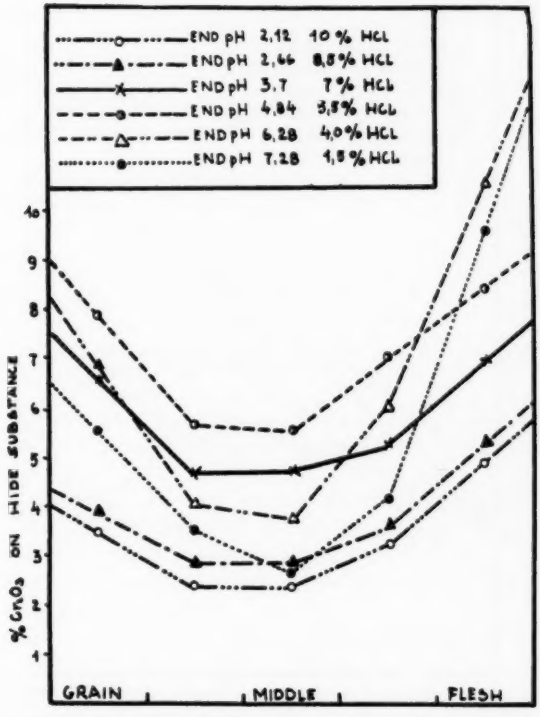
END pH 2,12 10 % HCL
END pH 2,66 8,5 % HCL
END pH 3.7 7 % HCL
END pH 4,84 5,5 % HCL
END pH 6,28 4,0 % HCL
END pH 7,28 1,5 % HCL
% Cr2O3 ON HIDE SUBSTANCE
GRAIN
MIDDLE
FLESH

FIGURE 17.—Effect of the end pH of the reduction bath on the stratographic distribution of chromic oxide. (Third series of experiments, without a pickle).

end pH (Figure 3). The distribution seems to be more uneven than in the former stratogram. At the bottom are the curves with the end pH of 2.12 and 2.66, both with a comparatively even distribution. At the top the curves with the end pH of 4.84 and 3.70 both show a rather uneven distribution. The curve of the end pH of 6.28 is deeper than the pH 4.84 curve signifying a lower chromic oxide value, and the curve with end pH of 7.28 indicates a still lower chromic oxide value, with both curves showing a very uneven distribution.

These relations are shown more clearly in Figure 18 where the chromic oxide values of each layer separately and of the unsplit leather are plotted against the end pH. The chromic oxide contents of all layers increases with increasing end pH up to a maximum which in most layers is about pH 5, while above this pH the chromic oxide decreases again. Only the flesh sides show an increase up to pH 6, and decreases above this pH.

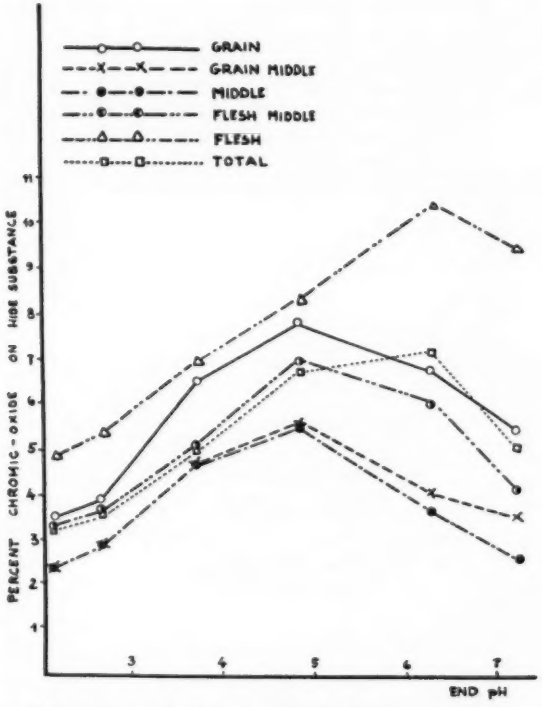

FIGURE 18.—Effect of the end pH of the reduction bath on the chromic oxide content of the separate layers and the unsplit leather. (Third series of experiments, without a pickle).

The small increase of the chromic oxide in the unsplit leathers between pH 5 and 6 is apparently due to the higher maximum for the flesh sides.

It should be remembered, however, that in all experiments the leathers were not shaved and what we call flesh sides would under factory conditions go in the shaving splits. Had the leathers been shaved, then the analysis of the unsplit leathers would also show an increase of the chromic oxide values up to a maximum at the end pH 5 and a decrease above this pH.

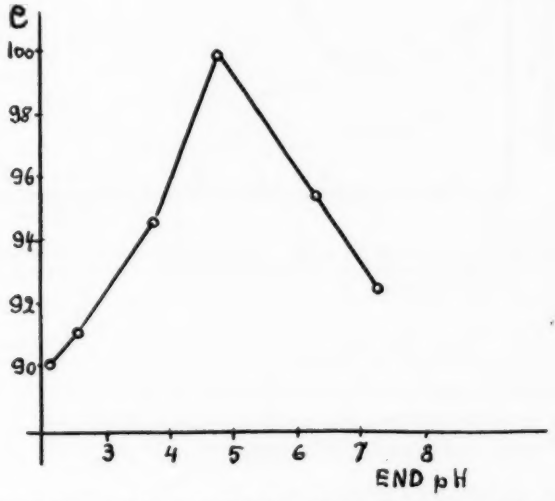

FIGURE 19.—Influence of the end pH of the reduction bath on the shrink temperature (Third series of experiments, without a pickle).

As Figure 19 shows, the shrink temperatures of the leathers after tanning increase also up to a maximum at an end pH of 5 and decrease rapidly above this pH.

Figure 20 shows the difference between the chromic oxide of grain and middle of the unpickled leathers. We see an even distribution of the chromic oxide only within a narrow pH range, above an end pH of 3, small increases of the pH rapidly increase the difference in chromic oxide between grain and middle.

If we compare the difference diagrams in Figures 4, 12 and 20, we can say:

a-Leathers which were pickled and received a pre-reduction showed an even chromic oxide distribution for values of the end pH up to about 5.

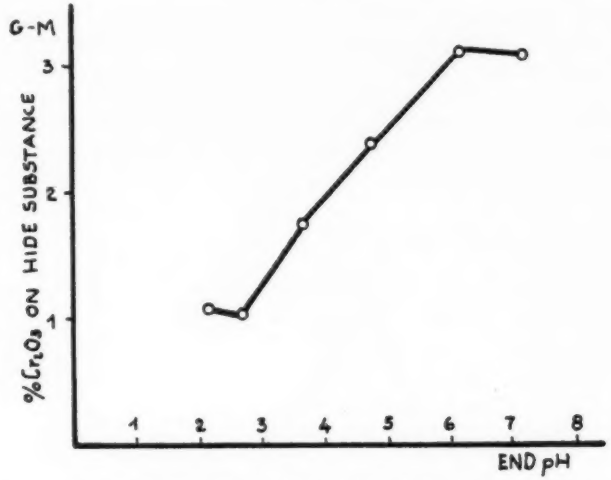

FIGURE 20.—Effect of the end pH of the reduction bath on the difference between the chromic oxide content of grain and middle. (Third series of experiments, without a pickle).

b–Leathers which were pickled without receiving a pre-reduction had a smaller range of uniform chromic oxide distribution up to an end pH of about 4.

c–The unpickled leathers had a still narrower pH range of an even distribution up to an end pH of about 3.

2. Effect of Masking Agents

In the unpickled leather the addition of sodium formate to the reduction bath also brings about a more even distribution of the chromic oxide. Figure 21 shows the stratogram of the unpickled leather with the addition of 3 per cent sodium formate to the second bath. The amount of hydrochloric acid was 7 per cent and the curve of the leather with 7 per cent hydrochloric acid without the addition of sodium formate is also given for comparison. Though the addition of sodium formate raises the end pH from pH 3.70 to 4.14 we find a lower content and a more even distribution of chromic oxide.

E. Fourth Series of Experiments

In this series of experiments we varied the amount of hypo used in the second bath. Everything else was kept constant and after bating and washing the skins were pickled and received the same first bath as in the other series of experiments. The second bath was carried out with 300 per cent of

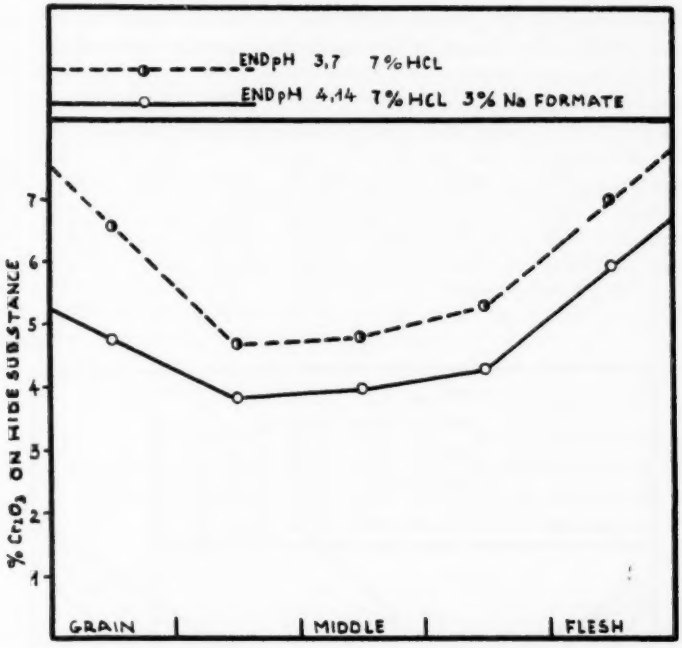

FIGURE 21.—Influence of the addition of 3 per cent sodium formate to the reduction bath on the stratographic distribution of chromic oxide. (Third series of experiments, without a pickle).

TABLE IX

Changes of pH in the Reduction Bath

(Fourth series of experiments, variation of amount of hypo)

Time	pH				
	5 Per Cent Hypo	10 Per Cent Hypo	15 Per Cent Hypo	25 Per Cent Hypo	30 Per Cent Hypo
1st addition HCl 15 min.	5.26	5.58	5.58	5.59	5.60
2nd addition HCl 30 min.	4.02	4.88	4.76	5.00	5.20
3rd addition HCl 45 min.	2.31	3.52	3.32	3.52	3.71
4th addition HCl 1 hour	1.56	2.34	2.66	2.92	2.98
1 hour, 15 min.	1.60	2.50	2.84	3.10	3.17
1 hour, 30 min.	1.56	2.56	3.00	3.13	3.25
2 hours	1.69	2.74	3.08	3.31	3.38
22 hours	1.67	2.90	3.14	3.33	3.47

water, 6 per cent hydrochloric acid and amounts of hypo varying from 5 – 30 per cent. The resulting leathers were then analyzed as in the former series of experiments. Table IX gives the changes of the pH during the reduction.

TABLE X

Effect of the Amount of Hypo on the Stratographic Distribution of Chromic Oxide.

(Fourth series of experiments)

Per Cent Hypo	End pH	Per Cent Chromic Oxide on Hide Substance						
		Total	Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
5	1.67	3.40	4.36	2.26	2.07	3.14	5.00	2.29
10	2.90	4.17	4.97	3.52	3.33	4.10	5.50	1.64
15	3.14	4.46	5.22	4.00	3.68	4.27	5.74	1.54
25	3.33	4.62	5.10	4.28	3.90	4.68	6.00	1.20
30	3.47	4.92	5.15	4.45	4.05	4.70	5.95	1.10

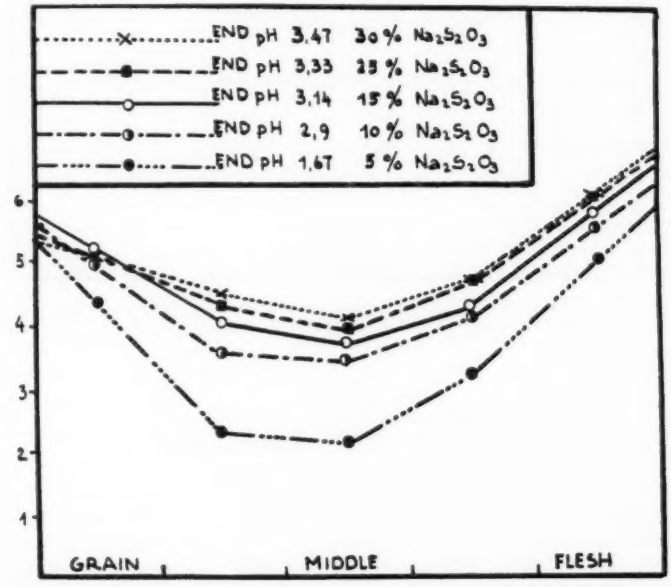

FIGURE 22.—Effect of the amount of hypo in the reduction bath on the stratographic distribution of chromic oxide. (Fourth series of experiments. Variation of the amount of hypo).

Stratographic Analysis of the Leather

1. Chromic Oxide Content

Table X and Figure 22 contain the results of the analysis showing the stratographic distribution of the chromic oxide. In Figure 22 we see at

the top the curve with 30 per cent hypo, showing the highest chromic oxide values and an even distribution of the chromic oxide. The curve below with 25 per cent hypo indicates a somewhat lower content of chromic oxide. With 15 per cent hypo the chromic oxide content is still lower, and the differences between chromic oxide content of the grain and the middle are somewhat bigger. With 10 per cent hypo the chromic oxide content appears still lower and the distribution less uniform than with 15 per cent hypo. With 5 per cent hypo we see the lowest amount and a very uneven distribution of the chromic oxide. With increasing amounts of hypo the chromic oxide fixation is increased and the distribution of chromic oxide is more uniform. From these results it appears to be advisable to use an excess of hypo in the second bath and it is in fact the usual practice to work with a hypo excess.

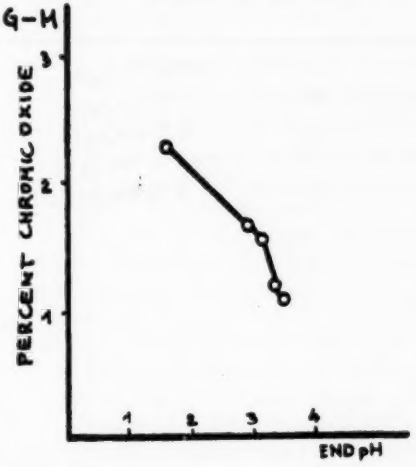

FIGURE 23.—Effect of the end pH of the reduction bath on the difference between the chromic oxide content of grain and middle. (Fourth series of experiments. Variation of the amount of hypo).

In the other series of experiments the pH depended on the amount of acid used. In the fourth series of experiments, however, the amount of acid used was constant and the pH was varied only by altering the amount of hypo. This changes completely the resulting difference diagram. In all the other series of experiments the difference between the chromic content of grain and middle increased with increasing pH. In the fourth series of experiments, however, the pH values depended only on the amount of hypo used, i. e., with increasing amounts of hypo the pH increases.

Figure 23 shows the difference between the chromic oxide of the grain and the middle against the end pH and we see that with increasing pH (increasing amounts of hypo) this difference *decreases*.

TABLE XI

Effect of Variation of Hypo on the Stratographic Distribution of Sulfur.
(Fourth series of experiments)

Per Cent Hypo	End pH	Per Cent Sulfur on Hide Substance					
		Grain	Grain Middle	Middle	Flesh Middle	Flesh	Difference Grain-Middle
5	1.67	0.56	0	0	0.57	1.26	0.56
10	2.90	1.37	0.72	0.59	0.79	1.56	0.78
15	3.14	1.13	0.55	0.41	0.68	1.20	0.72
25	3.33	0.66	0.12	0.13	0.33	1.10	0.53
30	3.47	0.34	0.10	0.05	0.23	0.70	0.29

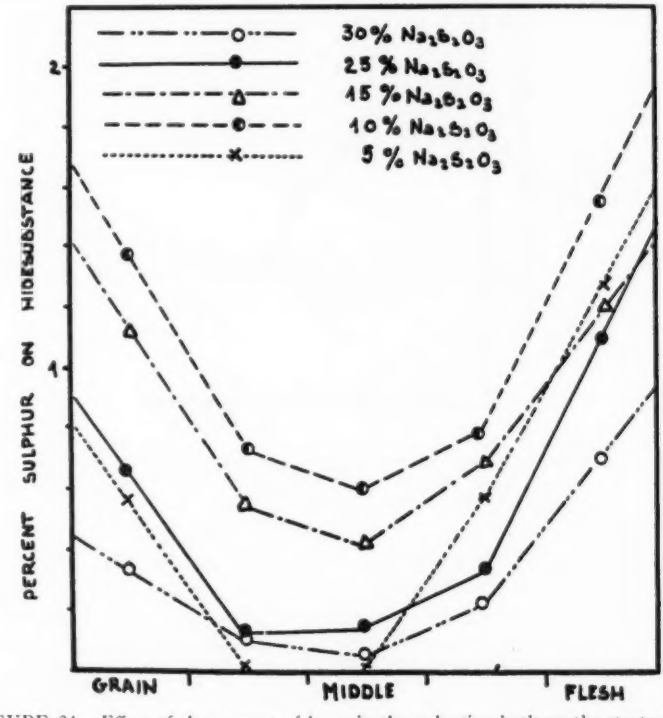

FIGURE 24.—Effect of the amount of hypo in the reduction bath on the stratographic distribution of sulphur. (Fourth series of experiments. Variation of the amount of hypo).

2. Sulfur Content

Table IX and Figure 24 show the effect of varying amounts of hypo and a constant amount of hydrochloric acid (6 per cent) in the reduction bath on the stratographic distribution of sulfur. We see with 30 per cent of hypo low sulfur values and an even distribution. 25 per cent hypo shows somewhat higher sulfur values. The curve with 15 per cent hypo indicates again higher amounts of sulfur and on top of the diagram is the curve with 10 per cent hypo, both curves show a rather uneven distribution of the sulfur. The curve with 5 per cent hypo has no sulfur in the middle layer, it is only present in the grain and flesh side, especially in the latter. From these results we can state: If the amount of hydrochloric acid is kept constant (6 per cent in this case), then we get, with large amounts of hypo, low values of sulfur and an even distribution. With smaller amounts of hypo the sulfur values are higher and the distribution is uneven.

F. Conclusion

Many of the processes which have been in practice for a long time, seem to aim at an even distribution of the chromic oxide and the sulfur throughout the leather. These are the use of a hypo excess, the pre-reduction process, the observing of a certain pH range, the use of a pickle; these operations, as we have shown, work towards a uniform distribution. It is rather remarkable that the practical tanner worked out these operations without any knowledge of the vertical distribution of chromic oxide, but only by comparing the resulting leathers. The contribution which chemistry brings now is the use of masking agents during the reduction which greatly aids in effecting a uniform distribution of chromic oxide and sulfur in the leather.

A similar development occurred in the one bath tanning. There also operations which have been in use for a long time, were found by stratographic analysis, to work towards an even chromic oxide distribution. For instance, the observing of a certain basicity, the presence of neutral salts, the use of a pickle, the beginning of the tannage at a low pH which is slowly increased during the tannage. Also in the one bath tanning the addition of masking agents helps in bringing about an even distribution.

We hope we have given another example of the value of layerwise analysis in solving problems of leather technology and chemistry. At a future date we hope to be able to report on our studies of the first bath and of the connections between the first and second bath.

G. Summary

We investigated the reduction bath of the two-bath chrome tanning and its influence on the fixation and distribution of chromic oxide and sulfur in the resulting leather. We find the following:

1 - The addition of acid in the reduction bath lowered the pH; during the reduction the pH increased again, first rapidly and later more and more slowly. The pH of the bath after 22 hours, when the skins were taken out, was called the end pH.

2 - The chromic oxide content of the leather increased with increasing end pH of the reduction bath. The stratographic analysis showed that a reduction bath with a low end pH produces leathers with an even vertical distribution of chromic oxide, while a reduction bath with a high end pH results in an uneven distribution of chromic oxide.

3 - The effect of the pH on sulfur was found to be the opposite. Increasing pH of the reduction bath decreases the amount of sulfur in the leather. The vertical distribution of sulfur in the leather is uneven at a lower end pH and even at a higher end pH.

4 - When the skins received a pre-reduction process (dipping in hypo-acid solution) before the second bath, the upper limit of the pH range for an even chromic oxide distribution was extended from pH 4 to pH 5.

5 - Leaving out the pickle before the first bath lowered the upper limit of the pH range for an even chromic oxide distribution to about pH 3.

6 - The addition of masking agents such as sodium formate to the reduction bath brings about a much more even vertical distribution of the chromic oxide and the sulfur throughout the leather. The total amounts of chromic oxide and sulfur in the leather are, however, smaller.

7 - A variation of the amount of hypo in the reduction bath showed that an excess of hypo increases the amount of chromic oxide and evens out the vertical distribution of chromic oxide in the leather.

8 - An excess of hypo in the reduction bath decreases the amount of sulfur in the leather and brings about a more even distribution of the sulfur.

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A Model for Collagen Fibril Structure Derived from Small-Angle X-Ray Diffraction*

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In recent years investigations with x-ray diffraction at small angles [2-7, 11-14, 19, 27] and with electron microscopy [8-10, 15, 16, 19-26] have contributed information as to the colloidal organization of collagen. Careful application of the diffraction method has made possible the development of a basic model for the structure of the collagen fibril. The origins of the model have been described in a series of papers which feature the mathematical and physical aspects of the problems involved [3-7]. In this report are summarized the results of these studies, and certain consequences of the model for the x-ray diffraction and electron optical investigations are stated.

Fundamental understanding of the phenomena accompanying the tanning of skins and hides requires as an important element a knowledge of how the tanning agents penetrate the collagen fibril. Application of the theoretical model to a consideration of how phosphotungstic acid (PTA) penetrates collagen fibrils is given below. This "electron stain" is widely used in electron microscopy, and in its reaction with collagen offers certain similarities to the behavior of more orthodox tanning agents.

A Model for Collagen Fibril Structure

Remarks regarding the diffraction method. To understand the results of diffraction study one must appreciate certain general characteristics of the technique and the information derived therefrom. The simplest approach is to regard the diffraction method as an extension of microscopy to resolution of the small details which are available when extremely small wave-lengths of electromagnetic radiation (x-rays) are employed (*cf.* Figure 1). Direct images can not be formed, however, because of the difficulty of fashioning lenses for x-rays. The following contrasts with the familiar procedures of microscopy then appear.

Instead of direct images of the object of interest, diffraction patterns, normally available just above the objective of the ordinary microscope, are photographed in the x-ray case. The registered pattern is the summation of

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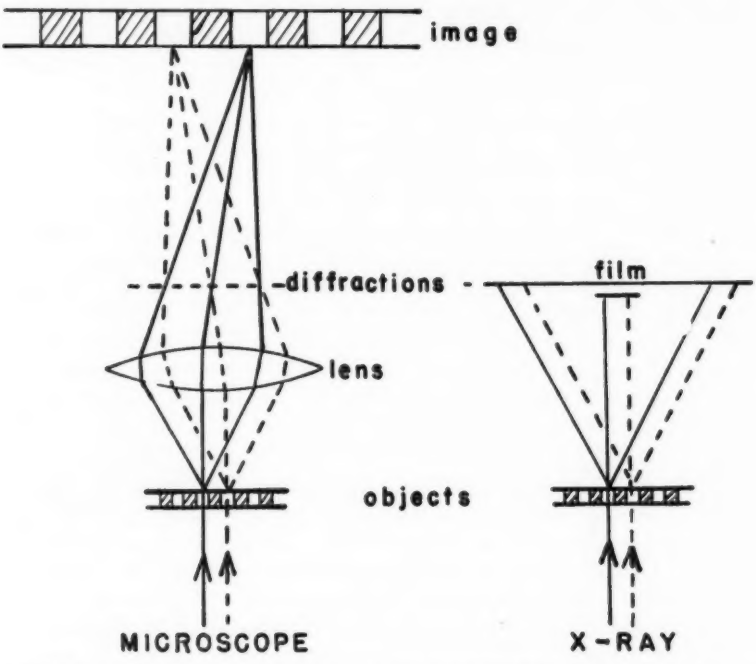

FIGURE 1.—Comparison of the microscope and x-ray methods of image formation. A beam of light incident from below upon a structured object is split into an undiffracted and deviated or diffracted components. The microscope lens (objective) combines these into both diffraction and direct images as shown, but the x-ray method can only record the former. A stop is interposed in the path of the central or dioptric beam to avoid halation of the film.

all of the diagrams which the elements (fibrils, in the case of collagenous tissues) would individually yield. The thickness of the specimen need not be small, as in microscopy, for if all fibrils are parallel the summation of their individual patterns is more intense than any one could yield. In practise, specimens are about one millimeter thick with collagen.

Definite study of the individual fibrils of a specimen is only possible with the diffraction method if all fibrils are nearly alike and well aligned. Among the collagenous tissues, tendons are most satisfactory in these respects. While most of the diffraction studies herein described have been done with kangaroo tail tendon, surveys of a number of different collagen sources [2, 14] suggest that the collagens of many vertebrate animals do not differ markedly in the respects which are important for the diffraction method, except as noted later.

The diffraction method must determine the angular deviations of the x-radiation, produced by interference between scattered waves emanating from the electrons of the atoms of the specimen. In microscopy large-aperture objectives must be used if small structural details are to be resolved, and similarly in diffraction work the evidences of small structures are to be observed at wide diffraction angles. Small diffraction angles, on the other hand, correspond to the small-aperture lenses of microscopy which are employed when large structural features are investigated. In other respects as well the diffraction pattern presents a peculiar sort of reciprocal image of structure. One important application of this is made below when diffraction line length is employed as a reciprocal measure of fibril diameter.

The incident radiation for diffraction study must be accurately controlled and limited as to its direction of approach to the specimen. Instead of the wide-aperture illumination furnished by microscope condensers, the x-ray collimator defines a narrow pencil of rays. This means a limitation of available energy and long exposures in obtaining the diffraction diagram. The problem of designing cameras with the greatest efficiency consistent with diffraction aims is particularly severe at small diffraction angles and has been studied by Bolduan and Bear [5], who described cameras suitable for collagen investigation. The entire range of sizes from the microscopic and colloidal (at small angles) to the atomic (at wide angles) are now covered by the x-ray methods.

The microscope objective recombines all diffraction in proper amplitude and phase to form an image of object structure, but the photographic plate and other recorders for x-rays measure only intensities of the diffraction effects. It is, therefore, impossible ordinarily to "focus" the x-ray diffraction pattern, by calculation, into an unique "image". An x-ray image is often secured by devising a model which satisfies certain immediately obvious properties of the diffraction pattern. One then revises the model until it is consistent with the observed diffraction and other pertinent physical and chemical facts.

Requirements for the model. Some of the major requirements which a model of collagen fibril structure must satisfy may be derived from existing facts disclosed by x-ray diffraction and electron optical studies:

(a) The collagen fibril has a large structure which is regularly repeated solely along its axis. Transverse to the axis structure is not found to be of repetitive nature until one considers much smaller spacings. The axial periodicity may be seen directly in electron micrographs, which show a characteristic cross-banded appearance [2 0]. Diffraction patterns show at small angles only a set of axially oriented diffractions related to a single fundamental fibril period of 600 to 680 A, depending on the condition of the sample [2]. This large spacing is represented on each diffraction diagram (Figure 2) by a series of equally spaced "layer lines" whose separation is inversely proportional to the period of the structure.

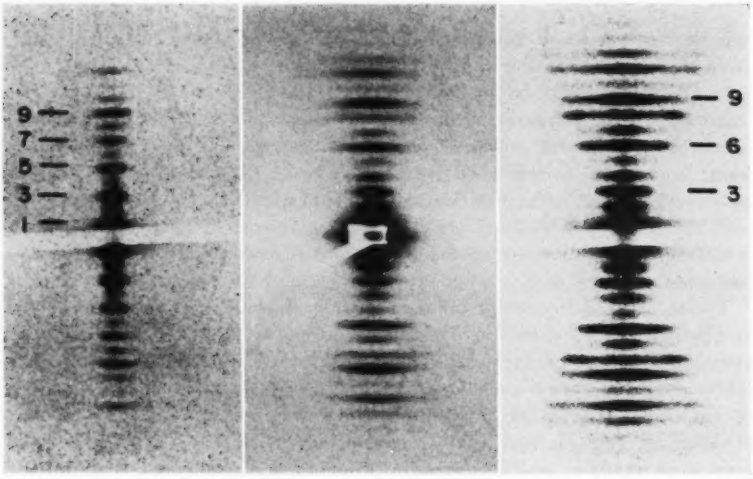

FIGURE 2.—Pinhole-camera diffraction patterns of kangaroo tail tendon: (a) with excess moisture present; (b) after soaking in water for two months, then drying under tension; and (c) after brief exposure to water and drying under tension. All patterns are magnified equally from their original size as obtained from a camera with 800 A resolution vertically (axially or meridionally) and 400 A horizontally (transversely or equatorially), using filtered CuKα radiation and a 15-cm. specimen-to-film distance[5]. Layer-line indices are indicated.

(b) Collagen fibrils often show a tendency toward longitudinal cleavage into thinner "filaments[20]" or "protofibrils[21]". This is apparent in many electron micrographs, but comparable effects may be observed in the diffraction diagrams. The latter evidence is observed as a spreading of diffracted intensity along individual layer lines transverse to the axial direction[6].

As is shown in Figure 2a, wet tendon specimens exhibit short lines closely applied to the axis of the diagram, indicating a strong coherence of the entire fibrillar structure. In this case the fibril may be described as a "smooth cylinder", whose longitudinal section is shown in Figure 3 (left) along with a representation of the diffraction pattern expected thereform. The constancy of diameter of the cylinder is reflected in the constancy of "length" of the diffraction lines, measured transverse to the general axis of the series[8]. The length of each line is inversely proportional to the radius of the cylinder.

Figure 2c shows particularly clearly that after drying of the material each diffraction lengthens transversely, with the increase in length becoming greater as lines become removed from the diagram center. This behavior indicates that the removal of water has introduced inter-filament, intra-fibrillar distortions which reduce the coherence of the structure[7]. The layer

lines near the center of the diagram represent larger features of axial structure and the relatively smaller filament distortions or displacements do not greatly influence the cross-section of the fibril over which the material scatters coherently to these lines. At non-central layer lines, related to finer structural details, the distortions are relatively more important and the line lengths increase to approach those which the individual filaments would produce if independently diffracting.

(c) The fibrillar structure possesses a feature which may be grossly described as "corrugation" [3, 7]. In electron micrographs [9, 23] this may be seen as a periodic variation in diameter, repeating along the fibril in close association with variations in inherent protein density and in the penetration of "electron stains". Particularly clear diffraction evidence of this characteristic is seen with the PTA-stained specimen whose diffraction pattern is reproduced in Figure 4a. The pronounced wing-like extensions of some of the layer lines provide evidence that the distortions of the last paragraph are more highly developed at some places along the fibril than at others. These give rise to the corrugated appearance, as is indicated further below.

Development of the model. To gain full advantage of the diffraction method, with its inherently great resolution and adaptability to quantitative study, it was necessary to proceed with detailed consideration of possible models in order to eliminate those which do not agree closely with the observed diffraction effects. Figure 3 depicts diagrammatically the types of model which have been most successful thus far. The greater complexity is encountered in the model for the dry collagen fibril [4] (Figure 3, right), but all of its features seem required to explain observed "line shapes", *i. e.*, the peculiar ways in which intensity is distributed along individual layer lines of such diffraction patterns as Figure 2c. The mathematical formulation of this model can not be adequately described in a single drawing, which must be supplemented with the following statements.

Along the axis of the model for the fibril occurs a periodic pattern of "perfect" and "imperfect" segments, as well as of the inherent material (or electron) density variations which all individual filaments are assumed to possess alike. This "mixed perfect and imperfect" model is best conceived relative to a hypothetical, completely pefect model, which would be the result of shrinking the smoothly cylindrical, moist fibril by dehydration without distortion in inter-filament relationships. In the processes accompanying actual dehydration, the imperfect levels arise where filament interaction and the removal of water permit irregular spacing of the filaments across fibrillar cross sections (radial distortion) and also axial displacement of corresponding locations on adjacent filaments from perfect matching transverse to the fibril axis (axial distortion).

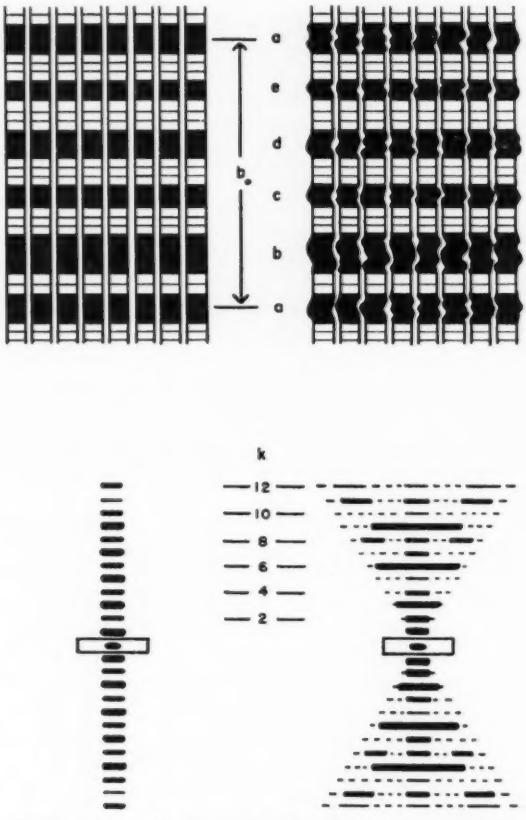

FIGURE 3.—Longitudinal sections through perfect (left) and mixed perfect and imperfect (right) models for collagen fibril structure. Eight filaments (protofibrils) are shown in each case, with the scale for filament thickness exaggerated relative to that for b_o, the axial period. Solid areas represent the distorted filament locations which constitute the electron optically visible bands a–e. Below each model are indicated the types of diffraction layer line each should exhibit at small angles. Diffraction components of perfection are the short lines shown everywhere for the perfect model and at some line centers for the partially imperfect model. The latter also shows components of longitudinal imperfection, e.g., the long line at k = 9, and components of radial imperfection, e.g., the pair of non-central maxima at k = 8. The choice of components represented is such as to approach the observed line shapes of Figure 2c.

The imperfection can be described only in a statistical way. The actual model assures the following characteristics: (a) that the axial and radial distortions need not be of equal magnitude at a given fibril level, but that

each remains statistically unchanged over the entire fibril cross section at that level; (b) that the parameters describing the distortion of either type are periodic functions of axial level; and (c) that the overall periodicity of perfection, imperfection and electron density remains the same all along the fibril, so that axially repeated segmental patterns of the fibril are statistically identical. One reasonably expects these details from *a priori* arguments based on the behavior expected of a structure which has regularity, as well as disorder, dictated by identical arrays of chemical material (one-dimensionally structured filaments), assuming that these have a tendency to match their structures during the process of transverse aggregation (fibril formation).

Standard mathematical procedures permit the most adequate evaluation of the scattering of x-rays by such a model for layer lines which are not too close to the center of the diffraction field. It is estimated, for example, that the first four layer lines of collagen diagrams are too central for trustworthy application of the theoretical relations regarding line shapes and lengths. Other limitations of the theory, such as the difficulty of ensuring that in the model the neighboring filaments will be distorted with due regard to each others space-filling properties, makes it impossible to regard the mixed perfect and imperfect model, in its present state of development, as a precise formulation for the diffraction behavior of actual collagen fibrils. Nevertheless, the degree to which this model is capable of accounting for the diffraction by dry tendons is remarkable.

All of the major characteristics of pattern 2c are satisfactorily explained by the model. The general expansion of layer lines is predicted to be closely a linear function of index, as is observed, and the details of intensity distribution or shapes of individual layer lines are expected and observed to be combinations of three general types of shapes: (a) a central, short peak of intensity, whose length is independent of layer-line index and which resembles the type of line exhibited by the simple smooth cylinder case ("component of perfection"); (b) a longer variety of intensity distribution, with maximal expression also at the line center but with length proportional to line index, arising from axial distortion ("component of axial or longitudinal imperfections"); and (c) non-central maxima of intensity, which show increased separation from the line center as the index increases and are derived from radial distortion ("component of radial imperfection").

The relative expressions of the three types of intensity distribution at a given layer line depend on "structure factors", which are functions of the specific ways in which the chemical material and the distortions are distributed along the fibril structure[4]. Involved at present is the validity of a general type of model which should be capable of accounting for the general characteristics of diffraction line shape without reference to details which may differentiate one particular structure from another of the same type. The more

difficult problem of arriving at complete models, capable of explaining the relative magnitudes of the structure factors, is still largely unsolved, though some suggestions regarding the structure factors will appear below.

Figure 3 shows, at the appropriate layer lines of the hypothetical diffraction patterns, simple representations of pure and compound shapes which approach those actually observed on the patterns of Figure 2. In particular, note that the existence of both central and non-central intensity maxima together on certain of the observed layer lines can be explained only by the postulation of regions of perfection and of radial imperfection in the collagen fibrils, and not by use of either kind of region alone.

Consequences of the model. Consider the pertinent quantities which serve to describe a dry collagen fibril in the condition corresponding to the pattern of Figure 2c. The most accurately derived dimension is the overall period, b_o, of the axial structure, in this case 627 A as determined from the separation between layer lines. The magnitude of the average fibril radius, R, was estimated [7] to be 1000 A from examination of the first layer line, which represents such large features of the structure that distortions are ineffective in altering its length very materially from that expected of a smooth, perfect cylinder with the same thickness as the actual fibril.

Filament radius, R_o, is not immediately calculable from features of the small-angle diffraction, but a diffractor like the model of Figure 3b should show equatorial diffraction at intermediate to wide angles from which the filament diameter may be measured directly. The pertinent diffraction [7] is taken to be the prominent wide-angle equatorial spot which is well known to represent a "side-chain" (Astbury [7]) spacing of 10 to 11 A for dry collagen. Consequently, $R_o \doteqdot 5.0$ A.

The theoretical development [4] defined certain parameters of distortion, σ_o, which express the mean magnitudes of the "root mean square" displacements between corresponding locations on adjacent filaments in imperfect regions of the fibril. Additional subscripts *a* and *b* were added to this symbol to distinguish, respectively, the displacements in radial and axial directions. The characteristic non-central maxima of radial imperfection, observed particularly at the eighth and eleventh layer lines of Figure 2c, occur at positions relative to the centers of the lines which indicate that the ratio $(\sigma_{oa}/\sigma_{ob})$ is about 1.85, or that the radial and axial displacements are of the same order of size. Their absolute magnitude can not be immediately determined, though one may reasonably expect them to be roughly of the same size as R_o.

In addition to possible differences in the structure factors for the components of perfection and of imperfection, the theory [4] indicates that the former component is favored over expression of either of the components of imperfection at a given k^{th} layer line by a factor

$$\frac{2R^2(k\pi\sigma_{ob})^4}{R_o^2 b_o^4}$$

Substitution of the estimated magnitudes of the various quantities shows that for the fifth to twelfth layer lines this factor is large (10 to 10^3). If the evidences of imperfection are comparable in intensity to those of perfection at these layer lines, the structure factors of perfection must in general be small relative to those of imperfection.

There are two chief ways in which the diffraction components of imperfection may be reduced in intensity relative to those of perfection: (a) by increasing the proportion of perfection in the fibril, which in the limit of entire perfection results in a specimen exhibiting only the diffraction components of perfection; or (b) by increasing the magnitude of the displacement in imperfect regions of the fibril, which according to the arguments of the preceeding paragraph also favors the intensification of diffraction by perfect regions relative to that by imperfect ones. Physically, the latter procedure corresponds to so enlarging the distortions at imperfect locations that the latter can no longer contribute appreciable coherent diffraction to the layer lines.

Because the two methods of destroying evidence of imperfection are observationally similar in result but almost diametrically opposed as to fundamental interpretation, one must seek criteria by which they can be distinguished. Note that in perfect fibrillar regions the filaments are all strictly parallel and will consequently tend to favor maximum length of the total fibril. Increase in amount of perfection by straightening filaments at imperfect regions should then result in an increase in overall axial period, b_o, while general increase in the filament kinking should shorten the period.

The former case seems to be well typified by the events resulting from rehydration of a dried collagen specimen, wherein diffraction evidence of imperfection disappears and the axial period increases from the 610–650 A, characteristic of most dried specimens, to the range 665–680 A typical of moistened samples. That a considerable increase in coherence of fibril structure accompanies hydration of collagen specimens is also indicated by the observation of Kaesberg, Ritland and Beeman [11], who found that moist specimens show much more intense small-angle diffraction than do dry ones.

Since dry specimens quite generally show shorter spacings than do moist ones, one may conclude that the former generally contain more imperfection. Minor differences in period can not, however, provide direct and reliable criteria for the indication of small differences in degrees of distortion. The large spacings of nearly dry specimens are often appreciably variable with small changes of humidity level [6], without correspondingly very obvious effects on layer-line intensities or shapes. This is understandable if some imperfect levels of the fibril are so badly distorted that they contribute little to layer-

line intensities while appreciably affecting the fundamental axial period.

The factor stated above also shows that diffraction components of perfection may be expected to persist to lines of higher index than can the components of imperfection. This behavior can be seen on the original films in cases similar to those of Figure 2c; the components of imperfection fade with increase in index until they are just barely visible in the neighborhood of the twelfth to twentieth layer lines when the central peaks of perfection are still apparent. Subsequently described cases of PTA staining also show this effect at lower indices (Figure 4b). Since it is often easier to obtain patterns with the features of the first twelve layer lines well represented, these generally receive most detailed consideration.

Examination of the model for the dry fibril suggests that introduction of distortion at a given locality decreases the density there as compared to that of a closely packed, perfect organization of the same material. Unless this locality has been left excessively deficient of content by the removal of water, its density decrease results in a local enlargement of diameter. Other substances, such as PTA and tanning agents, can most readily penetrate these regions of imperfection because there are faults in the structure for their accommodation. This sorption may also increase the imperfection and help spread disorder to neighboring, more persistently perfect localities.

The relation of these suggestions to the familiar banding and corrugation of collagen fibrils as seen in electron micrographs is obvious, but the novel suggestion emerges that the electron optically apparent bands are the imperfect regions of the fibrils, while the interband regions have relatively perfect structure. Available evidence shows that electron strains enter at the same regions (bands) that enlarged diameters occur [9]. The density differences at various positions along unstained fibrils are generally insufficient for resolved detection, although the details of diametral elevation appear in such instances after replication or shadowing. Further diffraction support for these relationships emerges below.

Effects of Phosphotungstic Acid Penetration

Specimen preparation. The general procedure used in the preparation of samples for the present investigation was the following: kangaroo tendon strips (2 g.) were soaked in water and introduced for 24 hours into 100 ml of solution containing prescribed concentrations of the solid $H_3PO_4.12WO_3.15H_2O$ at pH values obtained by adjusting with sodium hyroxide or hydrochloric acid. The PTA concentrations and pH values were selected to introduce graded amounts of PTA into the specimen. As is shown in Table I, within limits these two variables offer several paths whereby a given amount of sorbed material can be introduced. Although the diffraction effects are influenced in minor ways by the particular conditions used, for the purposes

of the present study the important variable is the amount of sorbed PTA attained.

After several washings and dialysis against distilled water to remove excess electrolyte the tendon strips were hung up in air to dry under tensions near to the maximum conveniently applicable without damage. The tension insured near perfection of parallelism of the fibrils, which is important for reasons given above. Methods of registering the diffraction patterns were those previously described [5].

TABLE I

Phosphotungstic Acid Sorption by Kangaroo Tail Tendon

pH*	PTA sorbed in samples†					
2.0	0.4	2.7	9.4	21.1	34.6	
2.5	0.4	3.0	8.0	20.0	31.0	
3.0		2.2	*7.5*	20.1	21.2	
3.6			5.6	7.2	*13.7*	
5.0	0.6	0.9	1.5	2.3	2.8	
6.0	0.3					
7.0	*0.44*	0.6	*1.3*	3.0	*3.9*	
9.0	0.0	0.3	0.2	0.2	0.1	0.0
10.0	0.0	0.0	0.0	0.1	0.0	0.2
	0.01	0.05	0.20	0.50	1.0	2.0

Grams of PTA in 100 ml of applied solution.

*pH of applied solution.

†The figures represent per cent of ash ($P_2O_5 \cdot 24WO_3$) in oven-dried specimens and were found in several instances to correspond closely to the loss of PTA from the supernate. Sorbed PTA is not removed by extensive washing. Itallicized figures identify the samples mentioned in the text.

Preliminary study with slit collimation. A survey of the general diffraction situation was first carried out by the use of cameras in which collimation of the incident x-ray beam was secured by slit apertures. Under these conditions cross-fire in the beam, parallel to the long dimensions of the slits and the lengths of the diffraction layer lines, permits rapid registration of patterns but does not allow distinction of the diffraction components of perfection and imperfection. Intensity comparisons were accomplished by registering each diffraction field on a pack of four consecutive films, over half of which was placed a Ni filter of known absorption for the Cu K_α radiation employed. Visual examination sufficed to yield estimates of relative line intensities suitable for present purposes.

The preliminary comparisons disclosed that added PTA is more effective in altering the distribution of diffracted intensity among the first dozen layer lines when the overall stain content is small rather than large. Consequently, samples were taken at increasingly large sorption intervals; 0.44, 1.3, 3.9, 7.5, 13.7, and 21.2 per cent sorptions were studied most extensively and sufficed to show the major effects.

Description of the observations is most conveniently made by dividing the layer lines into the three sequences of lines whose terminal indices are are the following: 1–3, 4–9 and 10–12. The mean intensity levels of these sequences decrease in the order given, but within each the relative intensities of individual lines were qualitatively as follows.

In the first sequence, the order of indices for decreasing intensity is 1, 2, 3 when less than about 14 per cent of stain has been introduced. This general decline of intensity with index carries over also into the fourth and fifth lines of the second sequence, as long as stain is below about 3.9 per cent. At higher sorptions this regularity is broken, so that at 21 per cent sorption the second layer line most notably falls to the point where it becomes even weaker than the third and higher lines through the ninth. In all cases the first order is the outstanding line.

A simple overall description for the second sequence can be derived by noting that somewhere between 1.3 and 3.9 per cent sorption (estimated at about 1.5 per cent) all of these lines have approximately equal intensities. The 1.3 per cent sample is nearly at this condition and has been the one found useful in studying line shapes in preliminary developments of the fibril model [6, 7]. Below this "crossover" point the sixth and ninth lines are prominent, as in unstained material [2], but immediately above it the fifth, fourth and seventh lines stand out. Eventually at the highest sorption the sixth line is again predominant, while the fourth, fifth, and seventh through ninth lines are of about equal intensity.

The final, third sequence shows a marked tendency toward constancy of relative intensities: the eleventh is always strongest, while the twelfth and tenth follow in that order at all PTA concentrations.

Study with pinhole collimation. The slit-camera patterns indicated the concentrations of stain which were strategic for pinhole-camera study of perfection and imperfection. The pinhole-camera patterns are shown in Figure 4, which with Figure 2c as an unstained control, presents a series capable of showing the major effects of PTA on collagen diffraction.

It is convenient to contrast each stage relative to the following components of layer-line intensity: (a) the component of perfection, which largely dedetermines the intensity at layer-line centers; and (b) the components of imperfection together, which contribute prominently to a wing-like, non-central development of layer-line intensity.

At small PTA sorption (1.3 per cent, Figure 4a) the most marked effect is the enhancement of the components of imperfection at certain of the even lines, so that the second, fourth, sixth and eighth lines now possess quite prominent wings extending from their centers. On the other hand, the odd lines with indices 3, 5, 7, and 9 are of similar, relatively short length and almost equal intensity.

The pattern at this stage has features which recall the diffraction by moistened specimens. Note that the even layer lines, which show the pro-

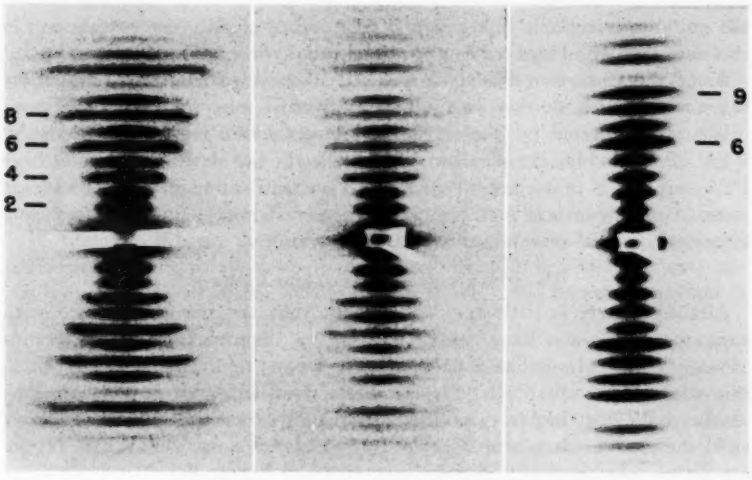

FIGURE 4.—Pinhole–camera patterns of dry kangaroo tendon samples containing (a) 1.3 o/o, (b) 3.9 o/o and (c) 21 o/o of sorbed PTA. All are at the same magnification and obtained like the patterns of Figure 2.

nounced evidence of distortion, are the ones that are faint in patterns from normal wet specimens. On the other hand the odd layer lines which are shortest with the dry stained specimen are the most intense for the normal wet preparation (Figure 2a).

As more PTA enters it increases distortion, eventually causing the components of imperfection to fade. At 3.9 per cent sorption, as seen in Figure 4b, the lines with even and odd indices in the range 2 through 9 still largely retain their respectively typical modes of intensity distribution; however, the non-central intensity of even lines has begun to fade, most noticeably at the higher indices (8 and 6).

The complex intensity changes noted above from the slit-camera patterns are functions of the redistribution of the diffraction components of perfection and imperfection among the odd and even layer lines and of the tendency of lines of high index to lose their components of imperfection as PTA sorption increases.

Eventually, at high sorption (21 per cent) diffraction evidence of imperfection has largely disappeared, as is seen in the relatively short, wingless lines of Figure 4c. That the disappearance of components of imperfection is caused, not by an increase of general perfection of order in the collagen fibrils, but by an excessive distortion in imperfect regions, is shown by the observations of the preceeding sorption stage and by measurement of the fibril structure period (b_o) at this final stage. While measurements of period

are not totally reliable indications of the degree of disorder (see above), in this case the period was reduced to the unusually low value 590 A.

Since the distortion has destroyed all coherent scattering by imperfect regions of the fibrils, the remainder must consist solely of the central components contributed by perfect fibrillar levels which resist penetration by PTA. Presumably, the return to prominence of the sixth layer line at high PTA sorption is in agreement with this view, since it suggests that at least some of the structural features, which were responsible for its outstanding intensity with the original, untreated dry specimens, are still intact.

Peculiarities of Kangaroo Tendon

Although there is little reason to doubt that the results obtained with kangaroo-tail tendon have general bearing on the structure and properties of many other mammalian collagens, there is one important respect in which this needs to be qualified. Experience with other (notably beef tendon) sources indicates that fresh collagenous tissues, when dried, do not always yield the clear evidences of imperfection visible on a pattern such as Figure 2c. Instead are normally obtained patterns like Figure 2b.

Detailed comparison of Figures 2b and 2c discloses, however, that the differences are ones of degree rather than of kind. Thus, the lines generally lengthen with increase in index, and ones which obviously possess components of imperfection in Figure 2c, are found in Figure 2b to streak out farthest from the center, though without clear non-central maxima. Indeed, it is something of a miracle that produces the periodic arrangement of order and disorder capable of diffracting as in Figure 2c. Even if the mixed perfect and imperfect model had been conceived before the diffraction pattern suggested it, one might have despaired of ever realizing the diffraction details any more perfectly than in Figure 2b.

Fortunately, the large supply of kangaroo tail tendon which had originally been adopted as a standard source for this work was capable of consistently supplying the necessary miracle. When the technical developments of diffraction method and of specimen handling had been perfected, the pattern of Figure 2c was immediately apparent. Failure to reproduce it with beef tendon led to attempts to ascertain experimentally whether specimens normally yielding Figure 2c could be made to show Figure 2b and *vice versa*.

The results were conflicting in many cases but seemed to indicate dependence on difficulty controlled variables involving the previous history of the sample, degree of hydration or swelling permitted prior to drying under tension, the actual tension then applied, etc. Kangaroo tendon samples, which had been in the dry state for an indefinite, very long period before examination, yielded the pattern of Figure 2b only after months of preconditioning by soaking in water, or after being more briefly swollen with acid or alkali. On the other hand, beef tendon produced the nearest approach to Figure 2c after several cycles of drying and brief remoistening.

Presumably the long-continued or cyclic drying prehistories favor the establishment of uniform predispositions of the filaments to become distorted so that consecutive segments of the fibrils are able to adopt statistically identical conditions, as is necessary for the development of the pattern of Figure 2c. Application of tension in the final process of orienting the fibrils for diffraction study is then unable to overcome the tendency for kinking of the filaments within the fibrils.

Notwithstanding these difficulties, the present kangaroo tendon samples have their advantages because of the possibility of detailed application of diffraction theory to their small-angle patterns. They give, in effect, particularly clear views of the events occurring when important alterations of fibril structure are produced.

Conclusion

The mixed perfect and imperfect model (Figure 3b) for the structure of the dry collagen fibril furnishes an illuminating insight into many of the observations of electron microscopy and small-angle x-ray diffraction. For example, as described above, the significance of the band and interband regions along the fibril begins to emerge.

The nature of the elementary filamentous units within the fibrils also becomes clearer. The present intrafibrillar filaments, a term employed in the theoretical development as non-prejudicially as possible, meet the specifications of the "protofibrils" originally postulated by Schmitt, Hall and Jakus[21] better than they correspond to the relatively thick (50 to 100 A) filaments of Schmitt and Gross[20], which undoubtedly are aggregates of the ultimate protofibrils.

The diffraction information furnishes compelling arguments against the view that the collagen fibrils are fundamentally arrays, nets or lattices of large globular, disk- or band-like particles. The largest structural spacing transverse to the fibril axis is that represented at the equator on wide-angle diagrams and corresponding to 10 to 11 A in dry collagen. This approaches so closely the value expected of the thickness of a single polypeptide chain that the use of the term particle ceases to have more significance than the very general one which could also be applied to a long filamentous unit. The length of the latter is not directly evident from the diffraction data, but studies of Scatchard *et al*[18] and of Salo[17] suggest that no very weak links, such as might terminate a polypeptide chain, are present within a length (800 A) which is the order of size of the observed large fibril period (600 to 680 A).

A logical extension of the above concepts is that the arrangement of imperfect bands and of perfect interbands should be determined fundamentally by the distribution of amino-acid residues along the individual protofibrils. Electron microscopy, in describing the band patterns, furnishes a rough view of this distribution, and it is desirable that the diffraction method should apply its greater resolving power to this problem.

The difficulties which might face the x-ray procedure arise from the following sources: (a) the fact, distinctly obvious in electron micrographs, that the pattern of bands and interbands depends on the direction of progression along the fibral (axial polarity); (b) the expectation that, in massive samples, as many fibrils will be oriented in a given direction as in the opposite one; and (c) the indication of the diffraction theory that the mixed perfect and imperfect model requires for its complete description several types of structure factor, related to perfection and the two types of imperfection.

Close examination of these sources of difficulty eliminates (b) from consideration, since each individual diffractor (fibril) should contribute to a given diffraction layer line exactly like an oppositely oriented neighbor. Consequences of (a) and (c) are more serious, however, because the axial polarity indicates that all of the many structure factors are completely indeterminate as to phase. Consequently, there is no immediately obvious hope of determining an unique x-ray image with the desired detail.

Nevertheless the present application of the mixed perfect and imperfect model to a study of PTA sorption shows that one can gain at least qualitative insight into the events occurring in a given situation. For example, the important conclusion has been reached that the electron stain enters primarily into the imperfect regions (bands). A survey of several other phenomena of this type will be given subsequently, along with examination of the concomitant events at wide diffraction angles.

Particular importance attaches to the phenomena observed in the neighborhood of the crossover sorption (1.5 per cent PTA). The amount of added stain is scarcely large enough to affect the internal fibrillar structure greatly, yet a most marked alteration of line intensities and shapes from the normal condition has occurred. Possibly this is due to a strong concentration of stain at particular bands, located perhaps once in every periodic segment of the fibril, in which case the structure factors would represent fairly simply the structure of the remaining parts of each segment, after a manner well known in diffraction theory. This phenomenon may prove of value in future attempts to circumvent the phase difficulty.

Another contribution of the diffraction observations is furnished by the similarities between the alternation of odd- and even-line intensities of the wet unstained collagen and the corresponding line-shape alternations of the dry stained preparations. These indicate a close relationship between the distribution of water in the normal moist fibril and of distortion after drying.

Summary

1. Models for the type of structure possessed by collagen fibrils are described (Figure 3). Each individual fibril consists of parallel protofibrils or polypeptide chains which tend to match their common pattern of chemical features transversely to their axial direction. The matching is best in hydrated material, but drying introduces distortion at various locations along the axis.

2. The models account for the bands (imperfect or distorted locations) and interbands (regions of perfect matching) described by electron optical studies, and they also explain several characteristic features of small-angle x-ray diffraction (Figure 2).

3. The sequence of diffraction events accompanying graded introduction of phosphotungstic acid into kangaroo tail tendon is described (Figure 4). The results indicate that this electron stain enters progressively into the imperfect bands, abolishing their contribution to diffraction, but that, up to sorption as high as 21 per cent, diffraction from perfect (interband) regions remains.

4. The kangaroo tendon samples proved peculiarly suitable for examination of the diffraction effects attributable to perfection and imperfection, apparently because of an appropriate previous history.

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X-Ray Diffraction Studies of the Penetration of Stains and Tans into Collagen Fibrils*

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A preceeding paper[3] described a model for the type of structure possessed by the collagen fibril and presented evidence concerning the mode of penetration into the fibril by phosphotungstic acid. The model was designed to account for small-angle diffraction but also offered illumination of some of the outstanding results of electron optical study. The general thesis was developed that a substance added to collagen most readily penetrates relatively unstable or easily distorted locations (electron optically visible bands) of the fibrils and leaves relatively unaffected the more perfectly integrated intermediate localities (interbands).

The results of the previous report are assumed throughout the present discussion, which describes additional experiments concerning the ability of reagents to interact with intact collagen fibrils.

ATTEMPTS TO STAIN SPECIFIC CHEMICAL GROUPS

The intrafibrillar filaments or protofibrils of the proposed model are very thin and have diameters expected of individual polypeptide chains. In preparation for the eventual possibility that the x-ray diffraction method may furnish information regarding the manner in which the amino acid residues are distributed along each molecular chain, some preliminary attempts have been made to tag specific residues chemically.

At early stages of the investigation the distortion phenomena were not known, so that it was thought that only slit-camera diffraction patterns need be obtained. After use of pinhole-collimated cameras led to a recognition that the problem was considerably more complex than originally conceived, this phase of the work was largely dropped in favor of development of the model. Nevertheless, a number of facts had been discovered which may be of use whenever this phase of collagen structure determination may be reopened.

Chemical Methods. The side chains which characterize the important amino-acids residues of collagen may be divided into four groups: those of basic reaction, as in lysine, hydroxlysine, arginine, and histidine; those of acidic

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character, as in aspartic and glutamic residues; other polar types, such as contain hydroxyl groups (serine, threonine and hydroxyproline); and the remaining non-polar groups of hydrocarbon character, as in glycine, the alanines and leucines, and proline. It is useful for diffraction purposes to tag relatively infrequent side chains. Because of their chemical inertness and the fact that they represent over half of the residue moles in collagen, study of the non-polar side chains is not promising. Investigation of the basic, acidic and hydroxylic polar side chains was attempted, and it was desired to provide means for studying each, either as a class or as specific individuals. Kangaroo tail tendon was employed because of its suitability for diffraction study [8].

As described by Salo [15], sodium hexametaphosphate (commercial Calgon) combines stoicheometrically with the basic side chains. The analytical data suggest that when collagen combines maximally with Calgon at pH 2.4 the composition of the hexametaphosphate is $NaPO_3$. $5HPO_3$. Of 6 atoms of P present only 5 are presumed able to join with basic groups of the protein. With this assumption the data for Calgon uptake correspond well with the results of other methods of estimating basic groups.

While Calgon presents one of the most satisfactory known tags for all basic groups, it is by no means ideal, since there is not a 1 : 1 correspondence between bound P and the number of side chains, nor is it certain in what form the phosphate is bound. Salo suggests that *monomeric* metaphosphate is bound because of the improbability that in collagen fibrils 5 or 6 basic side chains should be arranged in space appropriately for coordination with a single hexametaphosphate ion.

The uptake of Calgon can be controlled by adjustment of pH and added electrolyte concentrations, but the limitation of sorption to specific basic groups by this means does not seem feasible. More successful are methods which chemically alter the nature of these side chains selectively and thus prevent the sorption of metaphosphate at the altered sites.

Arginine, histidine, lysine and hydroxylysine are present in kangaroo tail tendon in the following respective amounts: 0.518, 0.055, 0.277, and 0.068 millimoles per gram of protein [13]. Deamination offers a means of removing the ϵ-amino groups of the lysines, and deguanylation might selectively modify the guanidine group of arginine. Both of these can be carried out on kangaroo tendon strips without destruction of fibril structure, as is shown by the ability of such specimens to yield satisfactory diffraction patterns after subsequent washing and air drying. Table I indicates, however, that neither treatment is completely specific in its attack on the side chains, though the deamination procedure confines its attack to the lysines reasonably well [14]. Deguanylation, with hypochlorite and hypobromite in highly alkaline solution, is particularly unsatisfactory, since more deamination of lysine occurs than deguanylation of arginine.

TABLE I

The Removal of Basic Groups of Kangaroo Tendon by Supposedly Specific Treatments.

Treatment*	Loss† (as percentage of total basic residues)			
	Calgon sorption	Arginine	Histidine	Lysines
Deguanylation	33	10.6	2.1	20.3
Deamination	38	3.9	1.2	32.9
Both	57	15.3	2.8	38.9

*Deguanylation was by the method of Highberger and Salcedo[8], deamination according to Thomas and Foster[17].

†Losses are for Calgon sorption[15] at pH 2.4, for arginine and histidine as determined by methods previously employed[12], and for the sums of lysine and hydroxylysine by difference between the Calgon loss and the total of the arginine and histidine losses, all figures having been reduced to residue equivalents.

In summary of the situation with respect to the basic side chains, one may use normal tendon specimens, in which all basic chains are accessible, or deaminated preparations, from which predominantly the ϵ-amino groups of the lysines have been removed. Sorption of Calgon at optimum pH (2.4) furnishes samples in which, respectively, either all or approximately the guanidine (also the relatively unimportant histidine) groups are marked by the phosphate. The lysines can be investigated by examining the differences between these two preparations.

Attempts to find satisfactory tags for the acidic side chains have been uniformly unsuccessful. Formation of salts with heavy metal cations or cationic complexes, such as those of silver and copper, is generally unsatisfactory, for the following possible reasons: Often these must be added at alkaline reaction, during which swelling introduces an excess of reagent beyond that equivalent to the acidic groups of the protein. In attempting to wash this out, it is found that the unions made specifically with the acidic groups are not sufficiently stable to prevent their dissolution also. It would appear that studies of this sort should be carried out with the collagen maintained in carefully chosen aqueous environments preserving a desired equilibrium condition.

Kangaroo tendon specimens may be maintained in moderately strongly acidic and basic environments and still be returned, after washing, to reasonably normal condition, as judged by their diffraction diagrams. It is reasonable therefore, to try various chemical procedures requiring these conditions, as in the esterification of the carboxyl groups of the protein with alcohols or of the hydroxyl side chains with added acids. Addition of methyl alcohol in 0.01 *N*. HCl has been used by Fraenkel-Conrat and Olcott[6] for esterification of protein carboxyl groups, but in present studies with collagen the structure of the fibril was disintegrated. Attempts to form a phosphoric ester with the hydroxyl groups of serine in collagen, after the manner employed by Riming-

ton [12] with casein (application of a chloroform solution of $POCl_3$ in an alkaline medium) did not succeed, apparently because of insufficient penetration into the collagen fibrils. The method of Reitz *et al.* [11] for the esterification of protein hydroxyl groups by the use of concentrated H_2SO_4 at -30°C. failed for a similar reason.

While the possibilities for tagging side chains were not exhausted, it appeared fairly clear that those dealing with basic groups of the protein were most promising.

Diffraction results. Methods of orienting the preparations and obtaining the diffraction diagrams were those previously described [4, 5]. The major effects to be seen on the diffraction diagrams taken at small angles were the following.

Calgon may be introduced into otherwise untreated kangaroo-tendon by methods described by Salo [15]. At pH 2.4 of the applied solution the sorption is maximal at about 3 per cent P content in terms of dry weight. Examination of the overall diffracted energy yielded after introduction of phosphate shows that the entire pattern is materially enhanced. The most notable relative intensity changes are experienced by the line with index 2, which fades appreciably with increase in P content. The sixth and ninth lines maintain their normal prominence, with the former somewhat increased. Figure 2b shows a pinhole pattern of maximally calgonized tendon, which is discussed further in the next section.

Because the change of lysine ϵ-amino groups to hydroxyls by deamination only changes NH_2 to OH groups it does not alter electron density distribution in the collagen fibrils. Consequently, the line intensities remain essentially those exhibited by untreated tendon. However, when Calgon is added maximally after deamination a change can be seen relative to the pattern of maximally calgonized, normal collagen. Figure 1 shows that the most prominent feature of this change involves the sixth layer line, which is reduced from its normal prominence and now is about equal in intensity to the neighboring fifth and seventh lines. The ninth line also declines somewhat.

Deguanylation, while not too specific chemically, should have minor effects on the electron density distribution of the fibrils, and corresponding alteration of the diffraction diagram occurs. This is noticed chiefly as a decline in the intensity of the fourth layer line, which becomes about equal to its neighbor, the fifth line. Further change after calgonization is exhibited as a decline of the third line to a low level of intensity, but the prominent sixth and ninth lines are relatively uninfluenced. Combined deguanylation, deamination and calgonization produce a normal dry pattern in most respects, but the influence of deamination may be seen in the characteristic decline in the intensity of the sixth line.

While the detailed interpretation of the intensity changes cited above is not immediately apparent, the rough correspondence of the observations to

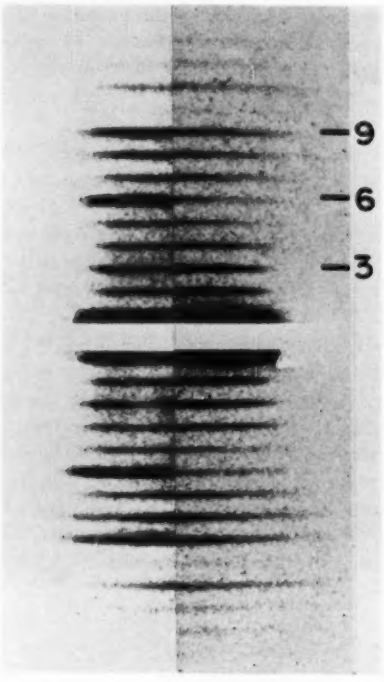


FIGURE 1.—Comparison of the slit-camera, small-angle diffraction patterns of maximally calgonized normal kangaroo tail tendon (on the left) and of similar calgonized but previously deaminated material (on the right). The integers are indices of pertinent layer lines.

the modifications expected in the chemical procedures is interesting. Few instances are known in which, as in these cases, a direct indication of a more or less specific chemical change of a protein has been observed on diffraction diagrams.

Effect of Tanning Agents

A detailed study, capable of examining all the facts that might be of interest in connection with the tanning problem, will be only slowly accomplished. At present are presented the results of a survey of some of the major tanning agents, designed to test in a preliminary way the usefulness of the small-angle diffraction method.

In order to benefit from the diffraction experience with kangaroo tendon the use of this material was continued. Samples were submitted to Mr. R. L. Sutherland of the A. C. Lawrence Leather Co., who kindly subjected them

to common chemical processes for chrome and quebracho tanning. Three levels of tanning were achieved for each method as follows: in the chrome tanning the percentages of Cr_2O_3 introduced were 2.57, 3.40 and 4.05, calculated on a moisture-free basis, and the "curl" temperatures of the products were 168, 184 and 194°F., respectively; the vegetable tan added was sufficient to produce the shrinkage temperatures 142, 156 and 166°F. In addition, maximally calgonized kangaroo tendon, prepared according to the method of Salo [15], was also studied.

Previously a number of patterns had been obtained from time to time with slit cameras using chromicized rat-tail tendon and calf skin. These had been oriented as well as possible by tension applied to strips of the specimens during drying, and the results agreed with the later ones on kangaroo tendon as far as the slit-camera diagrams could show. Because the subsequent studies employed pinhole cameras, the results are more illuminating and form the basis of the present discussion. The separate series of chrome- and vegetable-tanned kangaroo tendon proved incapable of permitting very great distinctions within each series. Chiefly the results for the most highly tanned samples are described. Figure 2 presents the patterns for the chromicized, calgonized, and vegetable-tanned material.

Chrome tanning. Figure 2a shows most pronounced intensification at the third, sixth and ninth layer lines, whose indices are all multiples of three

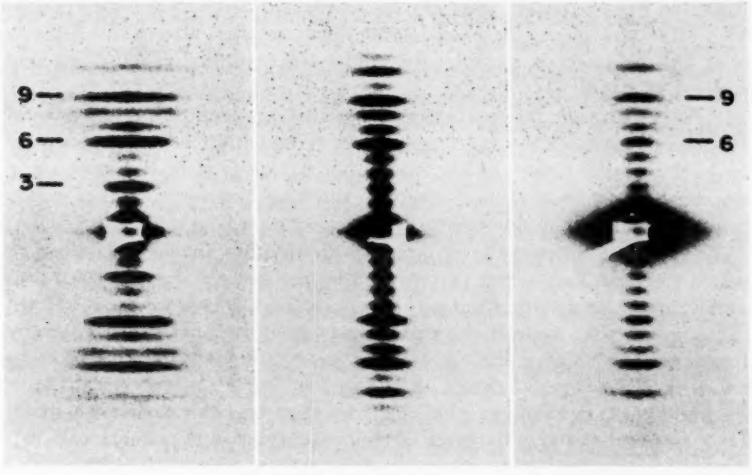


FIGURE 2.—The pinhole-camera, small-angle diffraction of (a) chrome-, (b) Calgon-, and (c) quebracho-tanned kangaroo tendon specimens mentioned in the text. Diffraction conditions were the same as for Figures 2 and 4 of reference 3.

Conparison with Figure 2c of the earlier report[3] shows that this has been attained, from the normal condition, not so much by marked alteration of these lines as by a noticeable depression of the second line and minor intensity changes for others. (In all such considerations, it is understood that the first layer line is always the strongest on the pattern and need not be specifically mentioned).

Similar tendencies seem to be characteristic of all chrome-treated samples which have been examined. This behavior was also previously noted for formaldehyde-treated rat-tail tendon[1] and to a lesser degree for heavily stained PTA samples[3]. Inferior development of the phenomenon may also be seen with the calgonized and vegetable-tanned specimens considered below.

A detailed interpretation of these observations would be premature, but the results of Schmitt and Gross[16] with chrome-tanned calf and goat hides are interesting in this connection. These investigators showed electron micrographs in which a six-banded structure of the collagen fibrils appears. If the bands they reported are paired as b_1, b_2; c, d; and e, a, it is found that the centers of gravity of the three pairs are fairly exactly separated by thirds of the overall period. In this situation one may expect strong diffraction at layer lines whose indices are multiples of three. Presumably the outstanding ability of the chrome-tanned specimens to show the 3, 6, 9 sequence of layer lines is related to their tendency to yield electron micrographs in which the band pairs are most exactly located at thirds of the fibril period. With other treatments the band relationships are often altered by displacement and splitting or recombination into different relative positions and numbers of bands.

If the bands are interpreted, as suggested earlier[3], to be locations of imperfection at which the added agent may particularly readily penetrate the fibrils, it becomes clear why the intense diffraction lines in this case owe a considerable portion of their intensity to the wing-like components of imperfection extending from line centers.

The general characteristics of intensity distribution among the lines with indices 1, 2 and 3 resembles that yielded by moist specimens, which always exhibit prominent odd lines and very weak even ones at low indices(see below). This suggests that some of the chrome may be introduced rather generally throughout the collagen fibril, as is water, penetrating into perfect regions as well as imperfect ones. Schmitt and Gross found that chrome-tanned fibrils, in addition to dark banding (invasion of imperfect regions), also have appreciably stained interband or background regions (entrance into perfect locations).

The pattern of Figure 2a shows an effect which can be expected according to the diffration theory, indeed might well be more often apparent than has generally been observed. The spread of intensity along layer lines is appreciably less with this chrome-tanned material than was encountered with plain and moderately PTA—stained samples[3]. The diffraction components of

imperfection in the latter examples showed about the same rate of increase of length as a function of line index, but in the present instance evidence of imperfection is crowded measurably closer to the axis at all lines of the diffraction pattern. The theory [2] relates this phenomenon to the ratio of the parameters of distortion, σ_{oa}/σ_{ob}. Estimates of this are derivable from the position at which the distinguishable non-central maxima of radial imperfection occur. Normally this ratio is found to be about 1.85, but in the chrome-tanned specimen it is close to 2.5.

The theory does not as readily permit evaluation of the absolute values of σ_{oa} and σ_{ob}, so that it is difficult to conclude which may have been most altered to change the ratio. The generally smooth contours of Cr-tanned fibrils described by Schmitt and Gross would suggest that σ_{oa}, related to radial distortion, is decreased, so that σ_{ob}, the axial distortion, must also decrease even more. According to this interpretation, the Cr-tanned fibril preserves an ordered structure on drying somewhat better than do most collagen specimens.

Calgon and quebracho tanning. It is difficult to conclude whether the patterns of Figures 2b and 2c suggest complete perfection of the tanned fibrils or whether the excessive distortion encountered with heavily PTA–stained preparations [3] is again in evidence here. The relative intensities of the layer lines are like those in the case of heavy PTA staining and might be taken in favor of the latter view, but other evidence is conflicting. For example, the fundamental spacings for these tanned specimens are normal for dry collagen material (*ca.* 640 A). They do not show the appreciable shortening encountered with heavily PTA–stained examples (to 590 A), but the 640 A spacings in themselves can be cited against complete perfection [3].

The 3 per cent of P introduced by maximal calgonization corresponds to about 8 per cent of metaphosphate, while the quebracho tanning may have been light, judging from the shrinkage temperatures of the samples. Thus, the excessive additions of material are probably not involved here to the degree encountered in the PTA case, though the differences expressed on a weight basis are more apparent than when stated as volumes, which would be the significant relation when distortion of structure is involved.

The diffraction lines in the present cases are unusually short, approaching those suitable for diffraction from entirely coherent fibril cross sections. One must conclude, therefore, that the lines are solely components of perfection, in spite of origin from material (kangaroo tendon) which normally shows marked evidence of imperfection. Wide-angle diffraction cited below, indicates that these tans have penetrated the fibrils to a considerable degree. Taking these facts into account, one concludes that, of the two alternatives presented above, the similarity of the present examples of Calgon and quebracho tanning to heavy PTA sorption is to be favored.

Evidence of stain or tan penetration into moist fibrils. Whenever water is present abundantly in collagen specimens its manner of penetration dominates

TABLE II

Summary of Small-Angle Diffraction by Moist Kangaroo Tendon Specimens.

Specimens*	Line Intensities†	Period (b_0)
1.3 per cent PTA-stained	1, 3, 5 vs 7, 8, 9, 12 s 10 m	671 A
3.9 per cent PTA-stained	1, 3, 5 vs 7 s 8, 9, 10, 12 m	670
21.2 per cent PTA-stained	1, 3 vs 2, 4, 5, 6, 7, 8 s 9 m	617
Deaminated and calgonized	1, 3 vs 5, 9 s 7, 12 m	671
2.6 per cent Chrome-tanned	1, 3 vs 5, 9 s 6, 7 m	662
Quebracho-tanned, "curl" temp. 166° F.	1, 3 vs 6 s 5, 7, 11 m	674

*The PTA-stained specimens are ones previously considered[3], and the others are identified in the present text.

†For each specimen the major lines (distinguished by their indices) are divided among the three levels of relative intensity: vs (very strong), s (strong) and m (moderate); other lines, through the twelfth in each case, are weak if not mentioned. The deaminated-calgonized preparation is not much different from untreated material[1,3].

the small-angle diffraction diagram. Nevertheless, addition of stains or tans is not without effect on the patterns. Table II illustrates this point with several of the specimens which have appeared above and in the previous paper[3]. The moist materials were photographed as sealed in thin-walled Pyrex capillaries. The hazards of breakage in the vacuum cameras and the difficulties of maintaining perfect orientation in such specimens caused these studies to be more troublesome than most, but a sufficient number of cases were obtained to permit suggestion of the following generalization:

(a) The diagrams show no clear evidence of imperfection, if allowance is made for the arcing of layer lines, produced by a small amount of disorientation which is difficult to eliminate completely. As the generally high values of b_0 indicate[3], the perfection is probably widely distributed along each fibril. A possible exception is the heavily PTA-stained specimen, whose fibril period is as short (617 A) as in many dry collagen samples, though obviously elongated by the water (from 590 A when dry[3]).

(b) When water enters collagen specimens there is invariably observed a tendency for intensification of certain of the diffraction lines with odd indices

and for depression of other even lines; this is always seen at the first three to five lines but sometimes may occur up to the ninth or tenth. Water undoubtedly enters all fibril locations (prospective imperfect as well as perfect), though probably not uniformly. The particular distribution which water adopts along the fibril is apparently responsible in large part for the alternation of odd– and even–line intensities with moist samples.

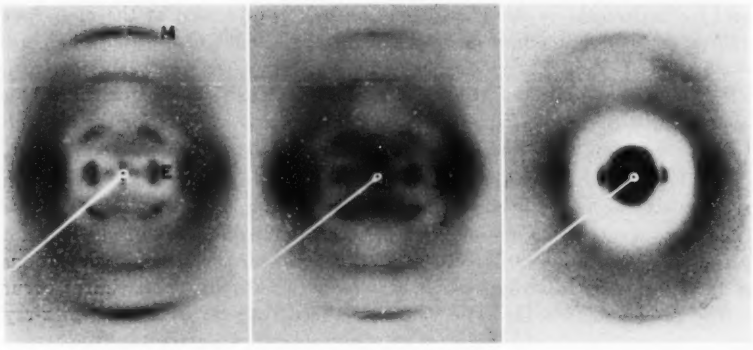
(c) The prospective imperfect regions (bands) are believed the ones which accumulate the most tan or stain [3], and as electromicrographs show [16] these are five to seven or more in number and distributed along the fibril. It is not surprising, therefore, that it is the fifth or higher layer lines at which deviations from the intensity alternations characteristic of normal wet specimens occur in the cases of Table II. The bands of added reagent, by their own x-ray scattering and/or by displacement of water normally contributing to scatter, impress upon the structure added details corresponding to fifths or less of the fibril period.

Wide-Angle Diffraction

In view of the evidences of considerable differences in internal organization existing in the fibrils of various dry specimens, it seemed desirable to subject these preparations to wide-angle diffraction study. This area of the diffraction field should be most sensitive to alterations in the spatial interrelations of the intra-fibrillar polypeptide chains.

In line with past general experience in this field all parts of the collagen wide-angle diffraction were found to remain persistently insensitive to manipulations which pronouncedly affected small-angle diffraction. Figure 3 illustrates the major types of wide-angle diagram secured from dry specimens exhibiting a wide variety of small angle diffraction. Pattern 3a is that normally yielded by untreated kangaroo and beef tendons and by samples which contained appreciable PTA stain [3]. Excessive amounts of stain make it difficult to record the pattern through the heavily x-ray absorbing deposit of PTA, but Figure 3c shows that at least recognizable features of the collagen diffraction are still apparent. Introduction of a tan (chrome, Calgon or quebracho) produces patterns like Figure 3b in which the intensity of diffraction E is more closely confined to the equator, as well as diffused somewhat.

The general thesis which has been developed earlier [3] and supported above suggests that if the distortions in imperfect fibrillar regions are sufficient to be effective in influencing diffraction at extremely small angles, they will be too severe to permit any appreciable degree of coherent diffraction from the imperfect bands to wide angles. In this event, the observed wide-angle diffraction is to be ascribed solely to the perfect or interband portions of the fibril. Since distortion following drying and the entry of strains and tans predominantly occurs at the bands, these influences can not markedly affect diffraction by the interbands In this view the insensitivity of wide-angle diffraction to alteration by the stains and tans is not surprising.



a b c

FIGURE 3.—Wide-angle diffraction patterns of dry (a) untreated, (b) chrome-tanned, and (c) heavily PTA-stained kangaroo tendon. M and E are, respectively, the meridional (2.86 A) and equatorial (10 to 11 A) diffractions which are outstandingly characteristic of collagen. Photographed at 5 cm specimen-to-film distance with Ni-filtered Cu Kα radiation.

Previous work demonstrated that the magnitudes of the wide-angle spacings remain relatively unaffected even with marked alteration of the large fiber period, and it was therefore suggested that the collagen wide-angle diffraction represents only a portion of the entire fibrillar structure[1]. It seems now possible to conclude that a host of collagen phenomena are consistent with this view.

Distortion is, however, relative, so that disarray of filaments within perfect regions of fibrils may still be noticeable at wide angles. In considering the patters of Figure 3 it must be kept in mind that they are from specimens possessing nearly perfect *fibrillar* orientation, as is disclosed by the straightness and lack of arcing of layer lines in the small-angle diagrams (Figures 2 and 4 of the previous paper[3] and the present Figure 2). Nevertheless, the diffraction E of Figure 3a is appreciably arced so that it is not confined solely to the equator. This observation may be interpreted as indicating a certain degree of disorientation of the polypeptide chains within the fibrils at the otherwise fairly perfect interbands.

Much of this minor distortion would be expected near boundaries or transitions between perfect and imperfect regions. If a tan spreads from an imperfect locality into a perfect one, it would increase distortion at the transitional zone, reducing the intensity of the contributions to wide-angle diffraction. This may explain, for example, the confinement of the diffraction E to the equator when tans are introduced.

K. H. Meyer[10] believed it difficult to consider the collagen wide-angle pattern as the product of a single diffracting component. A central system

of relatively sharp diffraction spots forms rudimentary row-lines and layer-lines with no obvious relation to the relatively diffuse and poorly oriented diffractions farther out, according to the usual expectations of fiber diffraction diagrams. After the roles of the two types of fibrils region, perfect and imperfect, were recognized in the present studies, the possibility arose that Meyer's duality of wide-angle diffraction might be related to the essentially dual nature of the small-angle diffraction. This is clearly not the case, however, for no evidence was obtained that different parts of the wide-angle diffraction vary significantly in relative intensities as specimens are examined with widely differing amounts of perfection and imperfection.

The view that wide-angle diffraction arises from the relatively perfect region of fibrillar structure will still allow for the possibility that Meyer's duality exists, since the two (or more?) aspects of wide-angle diffraction could arise from as many different interbands, each of which might have characteristic structure.

Alternatively the duality could conceivably exist within any one interband if the individual filaments should be of more than one type. In the theoretical development of the mixed perfect and imperfect model [2] all filaments were assumed identical for simplicity, but no detail of small-angle diffraction demands this as yet. Refinements to the model of the type mentioned in this and the last paragraph are not indicated at this time, nor is Meyer's suggestion clearly necessary.

Conclusion

Early studies of tanning by means of the diffraction method (reviewed by Highberger and Kersten [7]) often yielded conflicting or puzzling information regarding the action of tanning agents upon the wide-angle diffractions, which were the only ones then readily investigated. Although it was apparent that the tans do affect the parallel polypeptide chains of collagen fibrils, it now appears that the early observations dealt with relatively minor aspects of fibrillar penetration and that small-angle investigation is necessary to demonstrate the significant alterations of internal structure.

The chief difficulty which faces the x-ray method in translating the various small-angle observations into direct descriptions of the specific alterations in collagen fibril structure arises from the lack of information regarding the relative phases of the small-angle diffraction components [3]. Nevertheless, one can often gain some insight by noting the manner of distribution of diffracted intensity between the components of perfection and imperfection; the relation of these observations to the changes known to occur from parallel chemical or electron optical study; and the auxiliary evidence obtained from variations in the large fibril period and in diffraction at wide angles.

Among the most specifically recognizable features of small-angle diffraction, which seem to bear some interpretable significance, are the following:

(a) Layer lines which are simple, of constant short length, associated with large fibril period (660 to 680 A), and alternating in intensity, with odd lines strong and even ones weak at the lower indices (k=1 to possibly 10), are associated characteristically with the general perfection or coherence of structure conferred upon the collagen fibrils by hydration. Some stains and tans, notably chrome, cause, even in dry fibrils, the intensity alternation at indices k=1 to 3 or 4, indicating a certain degree of replacement of water by the added substances.

(b) Lines whose intensities are progressively spread from the meridian as index increases, whose separations correspond to axial periods below 645 A, and whose overall intensities have lost the pronounced alternation are recognized as characteristic of dry fibrils in which the separate properties of the imperfect (band) and perfect (interband) regions may be distinguished. In these cases intrafibrillar polypeptide chain distortion is not so severe at the bands that the diffraction evidence of imperfection is lost.

(c) Dry specimens which show relatively short layer lines of fairly constant length, associated with axial periods below 645 A and with prominent sixth and ninth layer lines, have been observed in cases which appear to have received concentrations of stain or tan at the bands sufficient to have destroyed the diffraction evidence of imperfection. Heavily PTA-stained and the present Calgon- and quebracho-tanned specimens are examples.

(d) Corresponding to the fact that electron micrographs show five or more bands, distributed along the collagen fibrils and dependent on conditions of pretreatment, many of the most difficultly generalized details of the diffraction variation occur at the fifth layer line and beyond. The relation decribed above connecting the electron optically observed locations of the bands of chrome-tanned fibrils with the indices of the diffraction lines at which major intensity is developed offers the best example that the number and relative positions of bands are important in influencing the general tendency of such lines as the sixth and ninth to be prominent.

The suggestion of the last paragraph is of interest in connection with the observations on deaminated, calgonized material in which the removal of the lysine ϵ-amino groups is associated with a decline in the intensities of the sixth and ninth lines. Location of the lysines residues predominantly at one or more of the bands is suggested. Kratky [9], for debatable reasons, expected that the distribution of lysine should profoundly affect the intensity of the eighth or ninth line, and that the sixth should be closely related to the distribution of the aspartic acid residues. From this failure and because of previously stated [1] other reasons it would seem that a simple relation between chemical constitution and small-angle diffraction, of the specific kind envisaged by Kratky, is not likely to be maintained.

It is not excluded, however, that the bands of collagen fibrils may eventually be found to contain the highly hydratable acidic and basic side chains

which would be readily accessible because of the loose fibrillar structure at the bands. On the other hand, the inaccessibility of the hydroxyl polar groups to chemical attack without fibril disintegration offers the suggestion that these may be located at the resistant interband regions. Details of this sort can not, however, be offered with any great confidence at the moment.

Summary

1. An account is given of attempts to alter or tag specific side-chain chemical groups of the polypeptide chains of collagen (kangaroo tendon). Basic groups are most easily controlled, hexametaphosphate (Calgon) providing a useful tag and deamination a means for selectively removing the ε-amino groups of the lysines. Variations of the small-angle diffraction intensities are observed to accompany the chemical changes.

2. The small-angle diffraction by certain chrome–, quebracho– and Calgon-tanned tendon specimens are described. Correlations with electron optical and previous diffraction findings are discussed. Different stains and tans produce by no means the same results, though there are often interrelations.

3. When moistened the stained or tanned tendon specimens show predominantly the influence of water, which causes an alternation of small-angle diffraction intensities (odd lines strong, even ones weak). The presence of an added material is, however, apparent as a modification of this alternation at lines (fifth or higher) which are believed related to the distribution of the electron optically apparent bands along the collagen fibril.

4. Wide-angle diffraction of dry collagen is relatively insensitive to the addition of stains or tans. The evidence suggests that wide-angle diffraction is produced only by the relatively coherent interband locations of the fibrils, which resist penetration and distortion by the added substances, though not completely.

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ABSTRACTS

The Resistance of Leathers to Hot Oil and the Preparation of Leather Suitable for Oil Seals. By A. T. Hough. *J. Soc. Leather Trades' Chemists,* **34,** 138 (1950). Certain leathers were examined with respect to their resistance to deterioration by dry heat and hot oil. With suitable tannage vegetable leathers were able to withstand temperatures up to 175°C. for prolonged periods in oil. Heat resistance was lowered by the presence of moisture. Chrome leather shrank and hardened when heated in oil, but the tensile strength remained fairly satisfactory. It is suggested that chrome leather destined for seals should contain more chrome than the leather tested (5.5 per cent), and to avoid shrinkage it could be preshrunk by intensive drying, and then impregnated with wax to prevent its absorption of moisture. Retanning with quebracho would be advantageous in prevention of shrinkage and hardening but at the expense of tensile strength. Catechol tanned leathers were found to be more heat resistant than pyrogallol tanned leathers. The author feels that his investigations are incomplete as they did not include leathers of sufficiently low moisture content, a wide enough variety of leathers nor heavy chrome retanned leather of the type recommended.

Notes on the Base Exchange Resin Method for Salt Estimations. By H. Lee. *J. Soc. Leather Trades' Chemists,* **34,** 150 (1950). The author was able to obtain results more in keeping with the amounts of salt to be expected from the addition of known quantities to mimosa liquors. This was accomplished by modifications of the procedure of Burton and Harrison.

Note on the Relationship between Tan Content and Hot Water Solubles in Black Wattle Barks. By L. H. Bryant and P. J. Martin. *J. Soc. Leather Trades' Chemists,* **34,** 151 (1950). A large number of samples of wattle bark were extracted by the official method and also with boiling water for 3 hours, using 10 grams of ground bark and one liter of water. A regression of hot water soluble Y on tannin content X was then obtained by standard statistical methods. The corresponding correlation coefficient was found to be +0.945. A satisfactory estimate of tannin content can be obtained from any given hot water solubles result by the equation $X = \frac{Yo}{b} + (b\bar{x} - \bar{y})$, where X is the per cent tannin, Yo the per cent water solubles, b the regression coefficient, $\bar{x}$ and $\bar{y}$ the means of tannin and hot water solubles, respectively. The equation is most dependable when the hot water solubles lie between 65 and 40 per cent. The standard error of estimate at each of the limits of the range is ± 0.3 and ± 0.1 per cent, respectively.

A Low Temperature Conductimetric Elucidation of Chromium Sulfate Complex Ions. By S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists,* **34,** 186 (1950). Inasmuch as the slopes of conductimetric titration curves of chromium sulfate complexes at high

dilution were found to vary with the speed of titration, thereby making it inaccurate to calculate the extent of coordination of sulfate from these slopes, an apparatus was designed for carrying out the titration at 5°C. The rate of complex change was much reduced as compared with that at 25°C. The essential features of the equipment were the circulation of brine from a thermostatically controlled brine tank containing the titration beaker through the burette jacket which enclosed the lower half of the burette. The author drew a number of conclusions from his work as noted. (1) By carrying out conductimetric titrations at 5°C. instead of 25°C. it is possible to reduce the rate of decomposition of chromium sulfate complexes at M/4000 to a degree where rapid titration enables the slopes of the lines to be utilized for calculating the complex bound sulfate. (2) At this temperature the characteristic break in the titration curve of one third basic chrome sulfate solution no longer exists, indicating that this break is due to the drift of co-ordinated sulfate at 25°C. from the two thirds basic complex formed during titration at this high dilution. (3) Calculation shows that a freshly boiled 10 per cent solution of one third basic chrome alum contains about 80 to 90 per cent of the titratable sulfate in the complex, which suggests that, if the complexes are mainly composed of two chromium atoms per molecule, about 60 to 80 per cent will be unchanged and the remainder cationic. (4) The absence of four lines of different slope in the titration curve suggests either that the mobility of the complex is very close to that of the sulfate ion (which seems unlikely for a large non symmetrical molecule), or that the attachment of sulfate by a single co-ordination link to chromium is very unstable. (5) Three independent observations suggest that the six numbered ring formed by sulfate with two olated chromium atoms is more stable than the four membered ring formed by a single chromium atom with the sulfate group. (6) Conductimetric titration curves obtained with chrome alum solutions boiled at various concentrations show that the characteristic breaks, due to the drift of sulfate from the complex at 25°C. are again absent at 5°C. Calculations of complex bound sulfate from the slopes of the curves give somewhat higher results than those of Atkin and Chollet, using the benzidine hydrochloride method, indicating that alkali probably has a greater affinity for the non-complex bound sulfate, which is titrated preferentially in the early part of the curve, thus giving a higher slope from the 33 per cent basic point onwards. (7) The results of Atkin and Chollet show that hydrolysis of chrome alum between 150 g. liter and 10 g. liter liberates two equivalents of sulfate from the complex for each OH group formed by hydrolysis. It is suggested that this is due to the instability of the single co-ordination link attachment of sulfate to these chromium sulfate complexes, so that either the sulfate is loosely attached by a single bond which is broken by benzidine sulfate, or else this single bond is displaced by a co-ordinated water molecule spontaneously. The former alternative would explain Plant's observations regarding the charge on the complex at concentration above 100 g. liter. (8) Tentative structures are suggested to fit the available information regarding the chrome alum and the basic chromium sulfate complexes.

Color Formation in Gelatin Manufacture. By J. N. Blake and F. H. Plaster. *J. Soc. Leather Trades' Chemists,* **34,** 177 (1950). While various agents have been regarded as causing the brown color when gluestock is hydrolyzed, and methods developed for overcoming it, the authors investigated the possibility of sugar as the cause of the color formation. The method used to determine the carbohydrate content of collagen and gelatin was based on the orcinol method of Sorensen and Hangaard. Values for the lactose content of gelatins of 0.40 to 0.68 per cent were found, and for air-dry split hide a value of 0.95 per cent was obtained. The sugar gelatin reaction was investigated and its color forming action demonstrated. The results suggest that the sugar present in the collagenous raw material might influence the formation of color in gelatin manufacture but no proof is put forward that it is the main factor.

Diffusion Studies on Dilute Aqueous Glycine Solutions at One and Twenty-Five Degrees with the Gouy Interference Method. By M. S. Lyons and J. V. Thomas. *J. Amer. Chem. Soc.*, **72,** 4506 (1950). The Gouy method for diffusiometry was applied to the measurement of diffusion coefficients of glycine in aqueous solutions of concentrations up to 4.8 grams of glycine per 100 ml. solution at 1.0 and 25°. Refractive index increments were calculated from the results of the same experiments, and density and viscosity data were also obtained for glycine solutions at 1°. The concentration dependence of the diffusion coefficients is not predicted correctly by Gordon's empirical equation, but the experimental behavior may be qualitatively explained by the suggestion of Robinson that glycine causes a breakdown in the ice-like structure of water.

The Kinetics of Chrome Tanning III. By P. S. Briggs. *J. Soc. Leather Trades' Chemists*, **34,** 165 (1950). The object of this paper is to amplify the work reported in Part I. (See *This Jour.*, **43,** 56 (1948) and to give the detailed results of some of the tannages from which the idea of the contact drop was developed in Part II. (See *This Jour.*, **43,** 570(1948). The usefulness of the exhaustion equation is further demonstrated and the alteration in its characteristics reflects the conclusion at which other workers have arrived from a study of the ultimate leather. In particular, the benefits of salt additions in regulating the course of tannage under different chromium concentrations is noted. Some criticism is put forward on current ideas of the role played by particle size of the chrome complex in tanning. The fact that the two to four chromium atom complex is small in comparison with the colloidal or semi-colloidal molecules encountered in vegetable tanning makes analogies between the mode of action in the two tannages misleading. Little is known of the increase in chemical activity of the chrome complex as its size increases with increment in basicity. By tanning pelt at the iso-electric point in place of the more usual pickled pelt, the chrome complex does not undergo disturbance and it is possible to compare chemical affinities by comparison with the half uptake periods or the momentary speed of combination. The evidence brought forward is held to favor the chemical activities of the chrome complexes being of greater importance in the rate of chrome tanning than is the particle size. Since in these tannages there is an excess of protein over chromium and the molecular weight range is comparatively small, the idea is propounded that uneven chromium distribution throughout the hide is due to rapid chemical combination rather than to slow diffusion. In considering the rate of tannage as affected by concentration as the one variant, despite irregularities arising from hydrolysis at high dilution, there appears to be an exponential relationship between the speed of tanning and the chromium concentration. A survey is given of a number of tannages covering a period of years in respect to their half uptake periods and the general relationship between the half uptake period and the concentration of the tanning float has been calculated.

Physical Testing of Leather Committee Report: Proposed Methods. By R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **34,** 253(1950). The Committee recommended for adoption as Official three methods, namely (1) measurement of buckle tear load, (2) measurement of indentation index, and (3) measurment of resistance to compression. The three methods are described in detail.

Investigation of Complex Formation in Solutions of Basic Chromium Compounds by means of Ionic Exchangers, Spectrophotometric Methods and Interaction with Collagen. By K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **34,** 259 (1950). The author summarizes his investigations as follows: From spectrophotometric investigations of dilute and concentrated solutions of basic chromium chlorides and sulfates, and by the ion exchange method, typical data of the composition and structure of

these compounds, in both the absence and presence of their respective sodium salts are given. Dilute solutions of chemically pure 67 per cent acid chromic chloride (0.4 g. eq.Cr. per 1.) contain only cationic chromium complexes, and even in concentrated solutions (8 g. eq. Cr. per 1.) practically all chromium in this form. These cationic complexes contain no complex bound Cl-groups. They exist in the form of hydroxo– or oxo-chromic complexes. The light absorption spectra of these solutions, measured in a concentration of 0.06 g. eq. Cr.per 1. are practically indentical, agreeing with results by the ion-exchange method. The same basic chromic chlorides containing sodium chloride (their composition corresponding to $Cr_2(OH)_2Cl_4 2NaCl$), contain only positively charged complexes in dilute solution. These are free from chloro-groups. In highly concentrated solutions, a few per cent of the total chromium is present in the molecular form (unchanged complexes): the greater part consisting of cationic complexes. These exist partly in the form of chloro-oxi-chromium-cations. The absorption spectra of the dilute and concentrated solutions of the chlorides, measured in a concentration of 0.06 g.eq.Cr.per 1., show marked differences; the optical density of the concentrated solution being very much greater than that of the dilute solution, measured at the same concentration. Further, the maximum of absorption of the concentrated solution is shifted towards the longer wave-lengths.

Dilute solutions of chemically pure 67 per cent acid chromic sulfate, without Na_2SO_4, contain only positively charged chromium complexes; with one sulfate group held by two atoms of chromium in the complex. About 90 per cent of the total chromium of the concentrated solution, 8 g. eq.Cr per 1., is present in the form of cations, the rest being uncharged. The light absorption spectra of the two solutions are practically identical. By the addition of one mole Na_2SO_4 per mole Cr_2O_3, yielding the compound of the general type: $Cr_2(OH)_2(SO_4)_2.Na_2SO_4$, the ion exchange results indicate that practically all chromium carries a positive charge in dilute solutions. On the other hand, concentrated solutions contain uncharged complexes as their main constituent (molecules of basic chromic sulfate). A few per cent of the total amount of chromium is present in the form of negatively charged complexes: the rest carrying positive charge. The extinction coefficient of the concentrated solution is considerably greater than that of the dilute solution, measured at 0.06 g. eq. Cr per 1. The spectrophotometric indications of very marked alterations in the structure of the chromium complexes of basic sulfate with increased concentration of chrome in the presence of nautral sulfates, confirm the results from the ion exchange reaction. By tanning for short periods (2-4 hrs.) with 67 per cent acid sulfate, $Cr_2(OH)_2(SO_4)_2.Na_2SO_4$, in (1) aged solutions and (2) solutions diluted to the final concentration immediately before use (0.4 g.eq.Cr.per 1), pelt fixes 50 - 100 per cent more chrome from the freshly prepared solution containing uncharged complexes as the main constituent, than from the aged solution, with equilibrium attained, consisting mainly of cationic complexes. The shrinkage temperature of pelt tanned in the former solution is a few degrees lower than that tanned in the aged solution. It is noteworthy that chrome fixation and the shrinkage temperature of pelt tanned in basic chromium sulfate devoid of sodium sulfate are practically the same whether aged or freshly prepared solutions are used. The same trend is shown by the basic chromic chlorides, with or without sodium chloride and irrespective of the chrome concentration. The difference in behavior of solutions of basic chromic sulfates of the regular chrome liquor type according to the chrome concentration is considered to be due to the uptake of uncharged, probably aggregated chromium complexes by collagen. Results of these and earlier investigations agree with the concept of chrome tanning as a multipoint attachment of the positively charged chromium complex to the negatively charged carboxyl groups of collagen, immediately leading to a direct association of the carboxyl groups with the chromium atom of the complexes by conversion of the labile electrovalent link, initiating the reaction, to the stable co-ordinate-covalent link of the final chrome-collagen compound. A supplementary fixation of non-cationic chromium complexes by collagen on its non-ionic groups occurs under certain conditions.

Reaction of the Natural Tanning with Boric Acid. By A. T. Hough. *J. Soc. Leather Trades' Chemists*, **34**, 278(1950). Beginning with the well known reaction of boric acid with certain organic compounds having adjacent hydroxyl, a study of the reaction was extended to phenol-formaldehyde condensates. Thus when a mixture of phenol and formaldehyde is heated with an alkaline catalyst and a sample is taken at intervals and titrated with a neutral borate solution using a pH meter, the curves obtained showed that whereas the unreacted mixture did not respond to the presence of the borate, as condensation took place and the time of heating was prolonged, so the increase of the quantity of condensate produced yielded a solution which became more and more acid upon adding the borate, the initial pH of 8.5 decreasing to 5.0. Of immediate interest to leather chemistry is the fact that the presence of the boric acid considerably influenced the amount of material fixed by collagen during tanning experiments, and also the quality of the leather. Leather tanned with the phenol condensate alone was thin and empty after samming and staking. When boric acid is added to the condensate a full skin of good feel is obtained on staking. Solution of commercial tanning extracts containing 2 per cent tannin were brought to pH 6.5 with caustic soda and then titrated with 2 per cent boric acid solution. Each material yielded a characteristic curve. A second series of curves was obtained wherein the initial pH was adjusted to 5.0. Gallic acid reacted most weakly. Sulfite cellulose was a close second. Increasing reactivity followed in the order: tannic acid, myrobalams, sulfited quebracho, mimosa, ordinary quebracho, reduncta and chestnut. It is apparent that boric acid does not react with all the tannophore groups in commercial tanning materials, but only with those having the correct spatial lay-out. This thought might be applied in studying the constitution of tannins, or in a practical way in the tannery to modify tanning practices and the quality of the leather obtained. Boric acid can react with many of the nontans such as pentoses, hexoses, hemi-celluloses and lignin derivatives. It is suggested that some consideration might be given to replacing strong acids in the hot pit liquors with boric acid. Further work is in progress to determine whether as good tannin fixation can be obtained with addition of boric acid and no heat as is gotten by the present procedure.

Regenerated Keratin Fibers from Wool. By F. Happey and R. L. Wormell. *J. Textile Inst.*, **40**, 855(1949). Through *J. Soc. Dyers and Colourists*, **66, 339**(1950). Methods are described by which wool is dispersed and extruded into a continuous-filament yarn with a β-keratin structure. The wool is dissolved by cold digestion with sodium sulphide solution, reprecipitated, redissolved, refined in cuprammonium, and again reprecipitated. Finally an approximately 35 per cent solution of the wet curd is made in either cuprammonium or ammonia, and after filtration, the yarn is spun into a salt bath, and stretched and hardened in two stages. The tenacity and extension of the final yarn are respectively 1 g./denier and 30 per cent at normal condition and 0.3 g./denier and 33 per cent wet. The stretching and hardening greatly improve the yarn properties, and X-ray photographs show that there is an increase in the crystallinity of the β-keratin which may be carried almost to the limit by stretching the finished yarns in steam. It is suggested that the process provides a means of regenerating a continous-filament β-keratin yarn from waste wool and other α-keratin proteins.

Para-Nitrophenol as a Fungicide for Leather. By F. O'Flaherty. *Lea. Mfg.*, No. 10, 5(1950). It has been found that 0.3 per cent para-nitrophenol gives leather superior mold resistance which is safe for use in close contact with the human skin. It can be incorporated into leather during oiling, by spraying, or by impregnation. Analysis of treated leather for mold resistance and para-nitrophenol content by previously published methods is described.

Extraction of Sumac. By F. L. Hilbert. *Lea. and Shoes*, 120, No. 15, 11(1950). Sumac is preferably leached in open wooden leaches, at a temperature of 110–140°F., although the author states that he has successfully extracted sumac leaves at 165°F. Proper leaching is dependent on the careful control of four factors, namely volume, circulation and temperature of extraction water, and time or duration of extraction. Sumac extract from domestic leaves, if produced at relatively low temperature, is quite satisfactory for the tanning of light colored leathers suitable for shoe linings and fancy leathers. Sicilian sumac is, however, generally considered superior to the domestic product.

Alpha-Monostearin and Sodium Stearate as Emulsifying Agents III. By H. H. G. Jellinek and A. Gordon. *J. Soc. Chem. Ind.* **69,** 235(1950). The action of sodium chloride, barium chloride, magnesium sulfate, aluminum sulfate, sodium nitrate and sodium sulfate on emulsions containing 1.0 per cent a-monostearin in water-white-oil and 0.5 per cent sodium stearate in water was investigated. The phase separation curves for the emulsions containing the univalent salts were similar. The emulsions were of the oil-in-water type; the oil separation became very rapid when a certain concentration of salt was reached. The bi- and tervalent salts caused phase inversion of the emulsions and precipitation of some of the emulsifying agents. The stability of the emulsions decreased with decreasing pH values and the structure of the emulsions became complex. At higher pH values very mobile and stable oil-in-water emulsions were obtained.

The Cuticle of Wool. By N. Gralen. *J. Soc. Dyers and Colourists*, **66,** 465(1950). Friction between wool fibers is smaller than friction between other fibers. This is explained by a thin fiber coating, the epicuticle, which was discovered by means of the electron microscope. The epicuticle is resistant to chlorine, acids, and enzymes. Alkaline treatment perforates it. The cuticle below the epicuticle consists of an intermediate layer, the exocuticle, and the scale substance proper, the endocuticle. The epicuticle prevents diffusion of large molecules, e. g. those of dyes. The Allworden reaction and staining tests for damage are explained by the existence of the epicuticle. It is easily damaged by mechanical treatments. Its removal gives an increase in fiber friction and thereby anti-felting properties. The importance of the frictional properties of fibers for spinning and wearing qualities is stressed. In the discussion which followed the paper it was brought out that the cuticle of wool is composed of β-keratin and that the bulk of the wool inside consists of α-keratin. This is of importance since the β-form has powerful interchain hydrogen bonding, resulting in much stronger structure than the α-form, in which most of the hydrogen bonding is within the same chain. It would appear as though wool has a tough outer shell and an elastic interior, an observation also noted with respect to hair.

On the Configurations of the Peptide Linkage in Proteins and Some Other Substances as Revealed by their Near Infrared Absorption Spectra. By M. Tsubol, *Bul. Chem. Soc. Japan*, **22,** 255(1949). The author made infrared absorption measurements in the 3-μ region of some materials, including egg albumen and horse serum, from which he deducted that the peptide linkage in proteins is of the trans configuration.

Size Distributions of Emulsions. By H. H. G. Jellinek. *J. Soc. Chem. Ind.*, **69,** 225 (1950). A systematic treatment of distribution functions of emulsions and their average quantities is given. An equation derived by Rossi expressing number-size distributions of emulsions is discussed; additional distribution functions and average quantities are derived for this case.

Alpha-Monostearin and Stearate as Emulsifying Agents II. Size Distributions. By H. H. G. Jellinek and H. A. Anson. *J. Soc. Chem. Ind.*, **69**, 229(1950). Size distributions were determined on emulsions containing a-monostearin in water-white-oil and sodium stearate in water at definite time intervals. The stability of the emulsions was found to depend on the concentration of the emulsifying agents and also on the mode of preparation of the emulsions. A homogenized emulsion was shown to be very much more stable than unhomogenized emulsions. The relationship between average diameters and specific areas with time was found to be approximately linear. Homogeneities and stability factors were evaluated for these emulsions. A mathematical analysis of the distribution curves was made.

The Oxidative Dyeing of Keratinous Protein Fibers. I. Dyeing of Wool with Colorless 2:4:5 - Trihydroxytoluene. By H. Burton and J. L. Stoves. *J. Soc. Dyers and Colourists*, **66**, 474(1950). Wool fibers can be dyed various shades of brown by aqueous solutions of the colourless 2:4:5 - trihydroxytoluene. Simultaneous treatment with various metal salts causes a pronounced darkening in the shade, which becomes almost black with ferrous iron. The brownish-black stain obtained by application of the trihydroxytoluene to living skin is attributed to the formation of a coordination complex derived from a thio. hydroxytoluquinone and iron; a similar process can thus be separated into two distinct stages with wool.

Subcuticle Membrane-A Recently Discovered Morphological Component of Wool Fiber. By P. Alexander and C. Earland. *Text. Research J.*, **20**, 298(1950). Through *J. Soc. Dyers and Colourists*, **66**, 495(1950). When wool is treated with a cold aqueous solution of peracetic acid for 25 hr., more than 90 per cent of the cystine present is oxidized and the wool becomes freely soluble in dilute ammonia except for a resistant fraction comprising 7–10 per cent of the whole. This fraction is membrane-like in form and is believed to represent the "sub-cutis", a sheath-like layer between the scales and the cortical cells in the fiber. The membrane is continuous, is resistant to chlorine solutions of any pH, and is a protein. It contains no cystine, but some cystic acid has been found. All the amino acids present in normal wool have been detected. Its resistance to alkali is similar to that of untreated wool. Its increased resistance to chemicals points to the existence of a covalent linkage, e. g., an ether linkage, not present in the rest of the wool. It may act as a selective membrane which in alkaline solution will have a negative charge and retard the diffusion of anions into the fiber.

Rate of Acid Sorption by Wool Fibers. By J. Lindberg. *Text Research J.*, **20**, 381 (1950). Through *J. Soc. Dyers and Colourists*, **66**, 495(1950). The rate of diffusion of mineral acids into wool fibers has been measured by dispersing short fibers (1–3 mm. long) in acid solutions and determining the decrease in concentration by means of a conductivity cell. Using the treatment developed by Crank (*Phil. Mag.* **38**, 794(1947); **39**, 140, 362(1948) for the sorption of a solute from a solution by a sorbing medium in plane sheet or cylinder form, the diffusion constant was calculated. The experimental curves of diffusion against time showed good agreement with the theoretical curves. It is shown that when wool is treated with substances known to impair the epicuticle of the fiber, e. g. alcoholic caustic potash, the rate of diffusion of acids into the fiber is increased.

Kjeldahl Method for Total Nitrogen. By P. L. Kirk. *Anal. Chem.*, **22**, 354(1950). The present status of the Kjeldahl method leaves much to be desired in spite of its wide use and tremendous value to industry, nutrition, physiology, biochemistry, and medicine. Fundamental research is still needed to elucidate and improve the digestion process for use

with different forms of nitrogen. The question of reducing and oxidizing agents other than sulfuric acid, and the matter of the proper catalyst, particularly require further fundamental investigation. Most significant is the rapid development and wide adoption of the micro and ultramicro forms of the Kjeldahl analysis. It is here that many of the most striking and significant developments are still to be expected, particularly in lowering the range of application and applying it to the exploration of minute biological systems, perhaps the living cell itself.

Dumas Nitrogen Determination Using Nickel Oxide. By W. Kirsten. *Anal. Chem.*, **22,** 358(1950). A description of modified and improved equipment.

Water Analysis. By S. K. Love. *Anal. Chem.*, **22,** 264(1950). A review of analytical methods that have been applied to the analysis of water and reported in the technical literature. Most of the papers on the subject were published during the past year.

Kjeldahl Microdetermination. By R. M. Silverstein and R. Perthel. *Anal. Chem.*, **22,** 949(1950). Three modifications were made in micro-Kjeldahl equipment to insure greater accuracy. An all-glass check valve was placed on the steam generator to prevent suck-back of material into the generator, or of distillate and receiving acid back into the distillation flask. A Goessman trap on the receiver containing the trapping liquid assured retention of the ammonia. The third modification is the use of 2 per cent boric acid in the receiving flask and titration with 0.01 *N* potassium biiodate solution.

Ultramicrodetermination of Nitrogen. By W. L. Doyle and J. H. Omoto. *Anal. Chem.*, **22,** 603(1950). To avoid bumping two heated metal blocks are used as digestion racks; one serves to remove most of the water, the second, to complete destruction at 250°C. The ammonia is received in potassium dihydrogen phosphate and titrated with acid to pH 4.6, using bromocresol green as indicator.

Paper Chromatography. By D. L. Clegg. *Anal. Chem.*, **22,** 48(1950). A review of the subject with 229 references. Paper chromatography has proved a versatile and useful tool in some types of work, notably biochemistry requiring analysis or separation on the microgram scale. Some procedures are suitable for routine work.

Chromatography. By H. H. Strain. *Anal. Chem.*, **22,** 41(1950). A review with 142 references.

Determination of Certain Nitrogen-Containing Functional Groups in Organic Compounds. By W. W. Becker. *Anal. Chem.*, **22,** 185(1950). Literature references and outline of procedures are given for the determination of the nitrate, nitro, diazo, azo, amino, amide, alkimide, and nitrite groups in organic compounds. The methods listed are specific for the particular group in question, but they may not necessarily be the shortest ones to use if no interfering constitutents are present.

Volumetric Analytical Methods for Organic Compounds. By W. T. Smith, Jr., and R. L. Shriner. *Anal. Chem.*, **22,** 101(1950). The authors discuss a number of volumetric analytical methods among which the following are of interest to the leather chemist: sulfides and disulfides, sugars, nitrogen, sulfur, lactic acid, aldehydes and amino acids.

Indicators. By I. M. Kolthoff. *Anal. Chem.*, **22,** 65(1950). Eighteen azo dyes are listed, along with their names, constitution, acid and alkaline colors, color change interval (pH), and oxidation-reduction property with respect to color.

Estimation of Amino Acids and Amines on Paper Chromatograms. By R. J. Block. *Anal. Chem.*, **22,** 1327(1950). Detailed directions are given for the preparation of one-and two-dimensional paper chromatograms for the separation of all the common α-amino acids and a number of nonvolatile amines. The quantity of color, as measured by a simple photoelectric densitometer, developed by ninhydrin or other reagents in each spot on these chromatograms is proportional to the concentration of the substance at the spot. This observation has been used as the basis for estimation of amino acids in less than 0.1 mg. of casein nitrogen.

Determination of Fluorine in Organic Compounds by Titration with Aluminum Chloride. By M. J. Gilbert and J. H. Saylor. *Anal. Chem.* **22,** 196(1950). Organic compounds containing fluorine are fused with metallic potassium and the fluoride ion separated by distillation as hydrofluosilicic acid. The fluoride ion is subsequently titrated with aluminum chloride, using eriochromcyanine R as indicator. Results with 25 organic compounds containing fluorine agreed closely with the theoretical.

Quantitative Determination of Amino Acids by Iodometric Titration of Their Copper Salts. By W. A. Schroeder, L. M. Kay and R. S. Mills. *Anal. Chem.*, **22,** 760 (1950). The method of Pope and Stevens for the determination of amino nitrogen in protein hydrolysates by means of the iodometric determination of the soluble copper salts of the amino acids has been reinvestigated, with the result that a better definition of some of the variables that made difficult the duplication of their results has been obtained. By the use of washed copper phosphate, fourteen of nineteen naturally occurring amino acids were determined with an accuracy of ± 1.0 per cent in quantities of 0.05 to 0.20 millimoles. Three gave high but consistent results, while histidine and cystine could not be determined satisfactorily. The deadstop end-point method was used to decrease subjective error of iodometric determination.

Mechanical Flaying in Italy. *Leather Trades Rev.*, **98,** 63(1950). A flaying machine, acting similarily to an oscillating safety razor protected by a comb-like shield, and operated pneumatically, has been introduced into a number of Italian abattoirs. It appears to be a forward step in flaying as judged from the improved take-off.

Antrycide. *Leather Trades Rev.*, **98,** 234(1950). The annual report of the East African Veterinary Research Organization records that some 60 cattle treated with the drug Antrycide were introduced into a fly area in Kenya Colony last September, and all but two died within four months, after developing trypanosomiasis in the first month. It was discovered that the trypanosomes had become resistant to the drug. It is recommended that more attention be now paid to the curative properties of the drug, and that local cattle be tested as to their susceptibility to it.

Adulteration of Crust East India Leathers. *Leather Trades Rev.*, **98,** 237(1950). Since there is nothing in the tanning of East India hides to warrant the presence of 18 per cent of glucose in the finished leather, it is believed that recent shipments showing this amount of glucose have been intentionally adulterated. Some leathers have also shown from 5 to 23 per cent Epsom salts. From time to time excessive grease has been reported, and and it is noted that this type of adulteration also continues.

American Type Chrome Retan Leathers. *Leather Trades Rev.*, **98,** 63(1950). The British object to vegetable retannage of chrome leather on the grounds that retannage contracts the leather, detracts from the natural silky feel of the grain, tightens the leather, and reduces its strength. On the other hand, practice of retanning is firmly established in the United States, and Sweden is producing chrome retanned shoe lining leathers, for which greater strength and fullness are claimed.

Tannin-Formaldehyde Resins as Adhesives for Wood. By L. K. Dalton. *Australian J. App. Sci.*, **1,** 54(1950). The tannins extacted from *Acacia mollissima, Callitris calcarata, Callitris glauca, Eucalyptus redunca, Eucalyptus consideniana* and *Eucalyptus crebra*, react with formaldehyde to form resins which have been examined as adhesives for wood. The rates of condensation of these tannins with formaldehyde have been assessed by measuring the gelation times. The adhesives produced with extracts from *A. mollissima, C. calcarata, C. glauca* and *E. crebra* set at moderate temperatures, forming with wood strong water resistant bonds. Adhesives prepared from the tannins from *A. mollissima* and *C. calcarata* set at room temperature to give bond with strength somewhat lower than those obtained from typical commercial adhesives, but having water resistance superior to the cold-set urea-formaldeyde adhesives.

Determination of Iron Content of Chestnut Extract. *Leather World*, **42,** 564(1950). A five gram sample of powdered extract, or a ten gram sample of liquid, is ashed, the ash dissolved in hydrochloric acid and the iron precipitated with ammonia. The precipitate is dissolved with hydrochloric acid, the solution made to volume and a known quantity to which potassium sulfocyanide has been added compared colorimetrically with iron standards similarily treated.

Fluctuations in the Incidence of Warbles in Hides in England and Wales. *Leather World*, **42,** 210(1950). Since 1940 sufficiently detailed statistical information on domestic hides in England and Wales is available to evaluate the decrease in warble infestation of the hides. The number of warbled hides is now only about half that of 1943. Warble manifestation is greatest in April–June hides and least in November–January hides. The greatest decrease appears in October–December hides, while the least reduction occurs in the April-July hides. The warble situation in France is also discussed, but here a feeling of pessimism exists because of the fact that progress in eradication of the warble is so slow.

Properties of Chemical Engineering Materials of Construction. *Ind. Eng. Chem.*, **42,** 2026(1950). This is the second section on chemical engineering materials of construction, the first appearing in 1948 in the above publication. It supplements, and in some instances, revises the data previously reported. The present report covers aluminum alloys, cements, elastomers, synthetic fibers, iron, mild steels, low-alloy steels, nickel and high-nickel alloys, plastics, hard rubber, tin and tin alloys, and the less common metals. Aside from giving the composition and physical properties of the materials, their resistance to atmosphere, water, acids and other chemicals are also tabulated.

The Charge of the Leather Surface. By G. Otto. *Das Leder* **1,** 81, 105, 133 (1950). The surface charge is an expression of the ability of the leather to react with polar substances. The isoelectric point of limed collagen is 4.9-5.2; above this pH value collagen binds anions and below this value, cations. Tanning is merely the taking up of charged bodies by the hide. Vegetable tannins are weak acids and are fixed to skin mainly by secondary valences. The surface charge of vegetable tanned leather is much more negative than that of isoelectric hide substance or skin in the weak acid region. Because of this

strong negative charge it attracts positive ions such as the cations of basic dyes. On the other hand it has less tendency to fix high molecular anions such as substantive dyes or sulfonated oils because its surface is already saturated with tannin anions. Sulfiting a vegetable tannin increases its negative charge. Leather tanned with sulfited extracts or syntans can be dyed with anionic dyes only if enough acid is used to lower the pH value below the isoelectric point. After dyeing such leather with acid (anionic) dyes, tanners often use a basic dye to obtain saturation in spite of the disadvantages of this type of dye. The conditions during mineral tannage are more complex. From the hydrolysis products of salts of chromium, iron, or aluminum, the hide may take up either complex cations or anions, depending on the acid radical. These cations or anions, if not stabilized by drying, are very reactive and may bind other anions or cations. The surface of mineral tanned leather is usually positively charged. To dye this leather with basic dyes it is necessary to first treat it with anionic (negatively charged) substances such as vegetable tannins, syntans, or an acid dye. The principal result of neutralization of chrome leather is a reduction of the strong positive charge so that negative dyes and fat emulsion particles are not absorbed too rapidly and therefore unevenly. Carbonate and borate are poor neutralizers because they do not prevent uneven dyeing. Suitable salt mixtures for neutralizing chrome leather are on the market, however. Retanned leather is usually made by retanning chrome leather with vegetable tanning materials. The chrome leather is positively charged and therefore takes up the vegetable tannin, which is negatively charged, with great rapidity so that it is desirable to repress this action. Mild tanning materials such as gambier or sumac may be used, or the positive charge may be reduced by the use of sulfonated oils or of acids that tend to form stable complexes with the chrome salt. Retanning vegetable leather with chrome is similar to the above except that the resulting chrome complex is more acidic. Dyeing may be too rapid and therefore uneven if the surface charge of the leather is too great. Even dyeing may be obtained by brushing on several applications of a weak dye solution or by using with the dye a substance having colorless ions with the same sign as the dye ions. Some of the products on the market for this purpose were made for textiles, and are unsuitable for leather because they contain a fat group and change the leather characteristics. Leather tanned with syntans has a negative surface charge, however, it can be dyed with anionic (negative) dyes if the positive groups of the collagen are first charged by lowering the pH value. The acid should not be added with the first addition of dye but later, in order to secure slower and more even take-up of dye. Substantive dyes are not usually satisfactory for anionic tanned leather. They are not soluble in the presence of acid, as a rule, and at higher pH values they attach by secondary valence to the same points as the vegetable tannin. They therefore find few points for fixation and penetrate entirely through the leather. The chrome leather surface has a positive charge and therefore little affinity for basic dyes. To secure even dyeing with anionic dyes a buffer such as "Tamole" may be used. Tamole is a neutral salt of tanning sulfo acids; it has active, colorless anions that combine with the leather in the same manner as the dye. Two types of Tamoles are available; (1) an acid dye type suitable for pastel shades, in which sulfo groups predominate and fixation is by principal valences, and (2) a substantive dye type which combines by secondary valences and is suitable for equalizing fuller tones. By use of these salts with colorless ions the affinity between leather and dye can be reduced so that the dye will penetrate through the leather. The natural dyewood extracts have a similar action for it has been shown by chromatographic methods that they contain both colored and colorless ions. Chrome velour leather must be staked and oiled before dyeing. Egg yolk is therefore used so that oil will not interfere with the dyeing; however if the egg yolk spoils it liberates phosphate which enters the chrome complex and so interferes with dyeing by reducing affinity for anionic dyes. Synthetic products do not have this disadvantage. Fat liquors are mostly emulsions with a negative charge and are unstable in acid solutions, however there are now available products with soluble cations. These usually contain pent-

avalent nitrogen. Upper leather requires more fat in the outer thirds than in the center but clothing leather should have the fat evenly distributed. By the use of proper agents the fat can be made to deposit either on the surface or evenly through the cross section of the leather. I.D.C.

The Chemistry of Chromium in Chrome Leather. By G. Otto. *Das Leder*, **1**, 153 (1950). After drying, chrome leather cannot easily be wet by water, it may no longer stand the boil test, and does not contain acid in the ionic form. If the leather before drying, is treated with compounds of dipole nature similar to water, such as polyglycerin or polyglycolic ether, it can be wet back. The behavior of chrome leather to dyes was studied to throw light on this complex process. Chrome leather neutralized with sodium bicarbonate does not take up basic dye if it is in the fresh condition but will take up basic dye after drying. Chrome leather will also take up basic dye if neutralized with a complex-forming, buffer salt mixture such as Neutrigan C instead of bicarbonate. The fact that both this type of neutralization and the drying of bicarbonate neutralized leather change the dyeing characteristics so that (1) there is more uniform dyeing with pure anionic dyes, (2) development of an affinity for basic dyes, and (3) a reduction in reactivity of chrome and chrome dyes (i.e., inner complex salts with deeper color do not form) indicate that in both processes there is formation of anionic chromium complexes. I.D.C.

Observations on the Determination of Insolubles in Tannin Analysis. By Hans Batzer. *Das Leder*, **1**, 156 (1950). A modification of the Wislicenus apparatus for determining soluble solids by the candle method is given. The method for standardizing the filter candles is not adequate. A thorough study of the method for insolubles or soluble solids is needed. Vacuum filtration should not be used; a syphon or a pressure system is better. I.D.C.

Tanning With Water Soluble Synthetic Resins. By Max Schwank. *Das Leder*, **1**, 177 (1950). The solubility and tanning behavior of melamin, methylolmelamin, and Artanol WL (Ciba) are briefly described. Directions are given for tanning with synthetic resins either alone or in combination with chromium. I.D.C.

Determination of Tannin in Vegetable and Synthetic Tanning Extracts. IV. The Accuracy of the Filter Method. By Oskar A. Müller and F. Stalder. *Das Leder*, **1**, 210 (1950). The filter method is known to give higher tannin values than the shake method. The following four possible causes for this have been suggested: (1) The wet hide powder used in the filter method is a better absorbent than the dry chromed hide powder used in the shake method, (2) Absorption of water of swelling by the dry hide powder may increase the concentration of nontannin and thus lower the tannin value, (3) The quality of the hide powder may affect the results, and (4) In the filter method the nontannin solution comes in contact with fresh hide powder. In a test with pine extract and Irgatan, prewetting the hide powder used in the shake method did not alter the results, so the first suggestion is not valid. The concentration of a nontannin filtrate was not increased by addition of more hide powder; rather it was decreased and the tannin value therefore raised. The quality of the hide powder should affect both methods in about the same way. In the filter method the first portion of the filtrate is discarded and in the shake method the soluble protein from the hide powder is precipitated by the tannin. To test the fourth suggestion, 8 filter tubes were packed with triple portions of hide powder and used for the analysis of 4 vegetable extracts and 4 syntans. The fitrate was collected in 14 25cc. portions, the first 4 beging considered pre-run fractions and the last 4 post-run fractions. Typical results expressed as purities rather than as percentages of tannin, were as follows:

Extract	Fraction 1	3	5	11	Official filter method	Shake method
Chestnut dry basis	43.8	82.6	83.1	82.3	81.0	—
Chestnut ash free	48.1	83.2	83.3	82.3	81.2	75.4
Quebracho dry basis	64.5	89.4	90.4	88.9	89.3	—
Quebracho ash free	71.3	88.5	89.1	87.1	87.9	84.0
Paratan 52 dry basis	47.0	65.7	60.3	46.4	51.8	—
Paratan 52 ash free	53.7	61.6	58.6	45.1	50.8	52.6

Purity as determined from fraction 1 was low. It reached a maximum with fractions 3 to 5, then decreased either slowly for vegetable tannins or rapidly for syntans as filtration continued. The low result with the first fraction was caused by soluble matter from the hide powder. When a carefully purified hide powder was used the first fraction gave practically a maximum purity value. The tannin removed by the filter method but not by the shake method has been called "semi-tannin" by Schröder. It has little astringency and no practical value as is shown by the following experiment. The tannin was removed from a quantity of chestnut extract by the shake method, then this solution was passed three times over carefully purified hide powder by the filter method. Only 0.044 grams of tannin was removed from a liter. Based on the hide powder used, this represents a tanning value of 0.8 per cent as compared with a value of over 60 per cent for the original extract. I.D.C.

Contribution on the Determination of Tannin in Vegetable and Synthetic Tanning Extracts. I. A Simplified Shake Method for Series-Tests and Its Use in a Succession of Tests with Varying Hide Powder to Tannin Ratios and Increasing Times of Retannization. By Oskar A. Müller and F. Stalder. *Das Leder*, **1**, 129 (1950). Various tanning materials are fixed at different rates by hide powder and this fact must be recognized in the shake method. Two series of tests should be made; one with increasing amounts of hide powder per 100 ml. of anlytical solution, and a second series in which the amount of hide powder and the volume of solution are kept constant but the time of shaking is increased from 0.25 hour up to 4 hours or more. The short time of shaking of 10 minutes was apparently chosen in order to give little time for the hide powder to release soluble matter to the solution and thus lower the tannin values. However, good hide powders will not give up enough soluble matter in 4 hours to affect tannin values. For vegetable tannins shaking for one hour is sufficient, although shaking for 4 hours does no harm, but for syntans it may be necessary to shake for from 10 to 18 hours or even more to obtain complete detannization. The analytical solution should not be diluted; it should contain 3.75-4.25 grams of tannin per liter. The pH of the solution is quite important. Syntans are adjusted to pH values suitable for special uses. All should be adjusted to 3.5-4.0 before analysis or the results will not be comparable. For some syntans it may be advisable to add mineral acid drop by drop during detannization if the pH value rises above 4.5 and the filtrate gives a positive test with gelatin-salt solution. Further information on the degree of detannization is given by testing the filtrates with 1 per cent tannin solution for dissolved hide substance and with gelatin-salt solution for tannin. The test with tannin is very sensitive but the gelatin-salt test is dependent on kind of tanning material, pH of the solution and quality of the gelatin. Only high quality, edible gelatin should be used. After swelling in cold water, it should be dissolved at a temperature not above 50°C. During the test the pH should be kept down to 3.5-4.0 and an observation made after 24 hours if no precipitate is noted earlier. In the simplified method, the detannization is done in thick-walled glass tubes 11 cm. long and 33 mm. in diameter, closed with rubber stoppers. After shaking, the solution and powder are pushed out with a close-fitting glass tube

(33-34 mm. diam.) into a funnel and round filter, 50 ml. of the filtrate is evaporated in porcelain on a water bath, then dried at 100°C. to constant weight. The residue is ashed at dull red heat and tannin and solubles are calculated to the ash-free basis.

II. Comparison of the Filter and Shake Methods, Including the Modified Shake Method. *Das Leder*, **1**, 159. Comparative results were obtained from 3 laboratories on extract samples of chestnut, quebracho, oak, and pine. All used the official filter method and 2 laboratories used shake methods but each laboratory used a different lot or make of hide powder. The filter method gave tannin values that were 5-7 per cent higher than the shake methods. The modified shake method gave satisfactory results. There was considerable variation in the insolubles values because some used paper and others, filter candles; these differences were reflected in tannin values. Agreement between laboratories was good when the sums of tannin and insolubles were compared.

III. Testing Hide Powder Quality. *Das Leder*, **1**, 160. Grasser's Handbook gives as a criterion of suitable hide powder that a residue of not more than 0.005 gram shall be found in 100 cc. of water after shaking 15 minutes with 6.0-6.5 grams of the hide powder. The official method provides only that the nontannin values from three different laboratories must agree when the powder is tested on four different tannin extracts of which one must be a cellulose extract. This is not sufficient. A series of detannizations with varying amounts of hide powder should be made.

The following seven hide powders were examined: (1) Freiberg No. 122 (1947), (2) Lyon EFT 3 (1948), (3) Kotva Czecho (1947), (4) Kotva purified by the author, (5) Freiberg No. 68B (1942), (6) England 12C (1938), and (7) No. 102 made by the author (1948). The first four were chromed, the last three unchromed. Soluble matter was determined by shaking 7 grams of air-dry powder with 100 cc. of water for one hour. The following results, calculated to the moisture-free basis, were obtained:

Powder Number	Ash Per Cent	Soluble Organic Matter Per Cent	Soluble Inorganic Matter Per Cent	pH
1	1.25	0.69	0.13	5.3
2	0.78	0.34	0.14	5.1
3	1.16	0.76	0.38	5.2
4	0.71	0.17	0.02	4.8
5	0.24	1.30	0.09	5.1
6	1.16	1.06	0.22	5.3
7	0.45	0.34	0.30	4.8

Low tannin values with chestnut extract were obtained if more than 3 grams of hide powder per 50 cc. of solution was used, except with powders Nos. 2, 4, and 7, which were low in soluble matter.

Basicity Determinations for the Analytical Characterization of Technical Chrome Tanning Liquors. By J. Plapper. *Das Leder*, **1**, 180 (1950). In the determination of acid in chrome liquors for calculation of basicity the chrome complex is not immediately broken up by the sodium hydroxide, especially if complex active organic acids are present. For this reason it is better to add an excess of standard sodium hydroxide solution, boil a few minutes, then "back titrate" with standard acid. If phenolphthalein is used for this back titration the carbonic acid is titrated to bicarbonate; that is, only half is determined. The "bromocresolpurple" method is as follows: Dilute an amount of the chrome liquor containing about

0.2 grams of Cr to 100 cc. in a liter flask with carbon dioxide-free water, add 15 cc. normal sodium hydroxide solution, boil several minutes using a Bunsen valve, dilute to 400 ml. with boiling carbon dioxide-free water, add a little bromocresol indicator and titrate with normal hydrochloric acid to the color change from strong blue-violet to weak bluish yellow. A second method, the barium chloride–oxalic acid method, is as follows: Proceed as in the first method to the point where the solution is diluted to 400 cc. after boiling with sodium hydroxide, then add to the boiling solution 15 cc. of 2 normal barium chloride solution and enough normal oxalic acid to decolorize phenolphthalein and titrate with normal sodium hydroxide to the first permanent pink color. By this second method all organic acids, including carbonic, are determined. The basicities of a chrome alum solution made basic with sodium carbonate, as determined by five methods, were as follows: bromocresol-purple method 33.6 per cent, oxidation method (Burton *J. Soc. Leather Trades' Chemists*, 1922 p. 92) 32.7 per cent, direct titration method 32.3 per cent, back titration method with phenolphthalein 15.9 per cent, and barium chloride—oxalic acid method – 18 per cent. Corresponding values for a sulfur dioxide reduced liquor were 36.9 per cent, 33.0 per cent, 32.2 per cent, 30.5 per cent and 19.5 per cent, respectively. The difference between basicities by the bromocreosolpurple and the back titration methods is a measure of the amount of weak organic acids including carbonic acid to the bicarbonate stage. The difference between the latter and the barium chloride–oxalic acid method is a measure of the amount of weaker organic acids, including the second dissociation stage of carbonic acid, that are precipitable by barium chloride. These methods will give information on the amount of sulfite and sulfur dioxide in sulfur dioxide reduced liquors. I.D.C.

PATENTS

Solubilizing Tanning Bark Extracts with Waste Sulfite Liquors. U. S. Pat. 2,505,818. K. T. Williams, Berkeley, and E. F. Potter, Richmond, Cal., assignors to United States of America. Appl. July 23, 1946. A method of solubilizing the insoluble material contained in an aqueous extract of western hemlock bark, comprising mixing the aqueous extract with a sulfite liquor produced during the cooking of wood in the manufacture of wood pulp and modified solely by having had its pH raised to approximately 5 and its alkaline earth metal ions substantially replaced by sodium ions, said extract and said liquor being mixed in such proportions that about three-fourths of the total dissolved material present in the mixture is derived from the extract and the remainder of the total dissolved material is derived from the liquor, and heating this mixture at a temperature of about 180°F. for about three hours.

Process for Manufacturing Artificial Chamois. U. S. Pat. 2,506,249. P. T. Tammen, Breda, Netherlands, assignor to American Enka Corp., Enka, N. C. Appl. Apr. 23, 1947. A process for manufacturing artificial chamois which comprises coating an open mesh fabric with a viscose solution and gelatinizing the same by heating in the neighborhood of 50°C., incorporating in a similar viscose solution a surface tension reducing agent of the class consisting of soaps, sulfonated oils, sulfonated alcohols and saponin and a vapor generating substance of the class consisting of low boiling hydrocarbons and halogenated hydrocarbons that generates a vapor at least at the temperature at which the viscose is coagulated, applying the viscose mixture to both sides of the gelatinized viscose fabric sheet and heating the laminated sheet in the neighborhood of 50°C. under atmospheric pressure whereby fine pores are formed in the outside layers of the sheet and finally regenerating the sheet in an acid bisulfate bath and desulfurizing.

Process of Increasing the Strength of Insolubilized Artificial Protein Filaments. U. S. Pat. 2,506,252. R. H. K. Thompson, Kilwinning, and D. Traill, Ardrossan, Scotland, assignors to Imperial Chemical Industries, Great Britain. Appl. July 26, 1945. A method for the production of protein filaments which comprises insolubilizing coagulated protein filaments by treatment with an acidic, saline solution of formaldehyde and, thereafter, contacting the insolubilized filaments for a time corresponding to about 30 to 45 minutes at room temperature with a formaldehyde solution of approximately 40 per cent formaldehyde concentration having a pH between about 8.6 and 10.4.

Process of Increasing the Strength of Insolubilized Artificial Protein Filaments. U. S. Pat. 2,506,253. R. H. K. Thompson, Kilwinning, and D. Traill, Ardrossan, Scotland, assignors to Imperial Chemical Industries, Great Britain. Appl. July 26, 1945. The method for the production of protein filaments which comprises insolubilizing coagulated protein filaments by treatment with an acidic, saline solution of formaldehyde and, thereafter, contacting the insolubilized filaments for a time corresponding to about 30 to 45 minutes at room temperature with a formaldehyde solution of approximately 40 per cent formaldehyde concentration having a pH between about 1.9 and 4.0.

Hog and Cattle Skinning Table. U. S. Pat. 2,506,532. W. J. Wilson, Morning Sun, Iowa. Appl. Feb. 25, 1949. A hog and cattle skinning device comprising a table having a table top including drainage means, a first set of transversely spaced longitudinal rollers, means for supporting said rollers on said table top, a second set of transversely spaced longitudinal rollers, and means for supporting said second set of rollers above said first set of rollers.

Process for Cleaning Animal Fibers to Prepare Same for Subsequent Use in Textile Operations. U. S. Pat. 2,508,406. M. Levin, Lowell, Mass. Appl. Dec. 27, 1946. In a process for cleaning animal fibers and preparing them for subsequent use in the manufacture of various types of cloths and felts, the step consists of subjecting said fibers to a mixture of sulfuric acid solution and a ketone effective to inhibit ionization of the sulfuric acid solution, said mixture containing not more than 20 per cent water.

Treatment of Keratinous Material. U. S. Pat. 2,508,713. M. Harris and A. E. Brown, Washington, D. C., assignors to Harris Research Laboratories, Washington, D. C. Appl. Oct. 7, 1946. The process for chemically modifying keratinous material to impart thereto enhanced resistance to the action of reducing agents, oxidizing agents and alkalis while preserving substantially unimpaired the mechanical properties of the keratinous material, which consists essentially in immersing the keratinous material for from 15 to 60 minutes in a liquid bath at a pH between 3 and 9 and at a temperature in the range 60–100°C., said bath containing a reducing agent for keratin which is inert to formaldehyde, to rupture disulfide linkages of the keratin, said bath containing more than 0.00045 mol per gram of keratinous material of free formaldehyde, whereby new stable alkylene cross-linkage between the peptide chains of the keratin are formed immediately upon rupture of the disulfide linkages.

Process for Treating Keratinous Materials. U. S. Pat. 2,508,714. M. Harris and A. E. Brown, Washington, D. C., assignors to Harris Research Laboratories, Washington, D. C. Appl. Oct. 7, 1946. The process for modifying a keratinous material to increase its resistance to attack by oxidizing agents, reducing agents and alkalis while preserving substantially unimpaired its mechanical properties, which comprises treating the keratinous material at a temperature between 60°C. and 100°C. and a pH above 7, in a liquid bath

containing 3 per cent to 100 per cent of the weight of the keratinous material of a reducing agent for keratin which is inert to alkylene dihalides, to rupture disulfide cross linkages of the keratinous material, said bath also containing more than 0.00045 mol per gram of keratinous material of an alkylene dihalide, whereby new stable alkylene cross linkages between the peptide chains of the keratin are formed immediately upon rupture of the disulfide linkages.

Antifoaming Compositions. Brit. Pat. 638,403. S. Stevens. Addition to boiler waters of a mixture of tannin (30-60 parts by weight), a long-chain ether of ethylene or polyethylene glycol (3-8), sodium carbonate (30-60), and glassy sodium phosphate (5-20) prevents foaming.

Gelatin Derivatives. U. S. Pat. 2,525,753. H. C. Yutzy and G. F. Frame, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y. Appl. Aug. 13, 1947. The method of preparing a gelatin derivative which comprises reacting gelatin with a dicarboxylic acid anhydride selected from the group consisting of phthalic, succinic, maleic and the chloro–, bromo– and sulfo–substituted anhydrides corresponding thereto in an aqueous system in which the pH is maintained at between 7 and 12 at a temperature of 30–70°C. for a non-degrading time of not more than forty minutes after the anhydride has been completely added.

Process for Dyeing Animal Hairs with Anthraquinone Vat Dyestuffs. U. S. Pat. 2,508,203. A. E. Weber, Ridgewood, N. J., assignor to Allied Chemical & Dye Corporation, New York, N. Y. Appl. Aug. 17, 1948. In a process for dyeing animal hairs with anthraquinone vat dyestuffs in reduced, alkaline vats, the step which comprises carrying out the dyeing in an anthraquinone vat liquor containing an alkali, an alkali metal hydrosulfite in an amount between about 1 and about 2.5 times the amount by weight of the alkali in the liquors, and a quantity of a neutral alkali metal salt between about 5 and about 50 grams per liter of vat liquor, while maintaining the vat at all times during the dyeing sufficiently alkaline to produce a slight to considerable color reaction with Clayton yellow test paper, and at temperatures between about 90°F. and about 125°F.

Surgical Gelatin Dusting Powder and Process for Preparing Same. Pat. U. S. 2,507,244. J. T. Carrell, Kalamazoo, Mich., assignor to The Upjohn Company, Kalamazoo, Mich. App. April 14, 1947. A sterile, substantially water-insoluble, non-antigenic, completely proteolytically digestible powder suitable for surgical lubrication consisting essentially of gelatin that has been hardened to the stage of substantial water-insolubility and that has thereafter been pulverized and subjected to heat treatment, which powdered material is completely digestible within approximately 6 hours in a 0.5 per cent aqueous pepsin solution.

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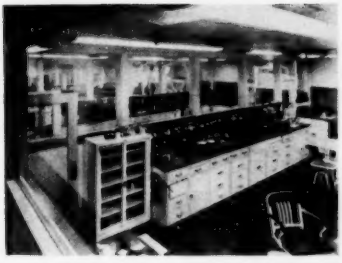

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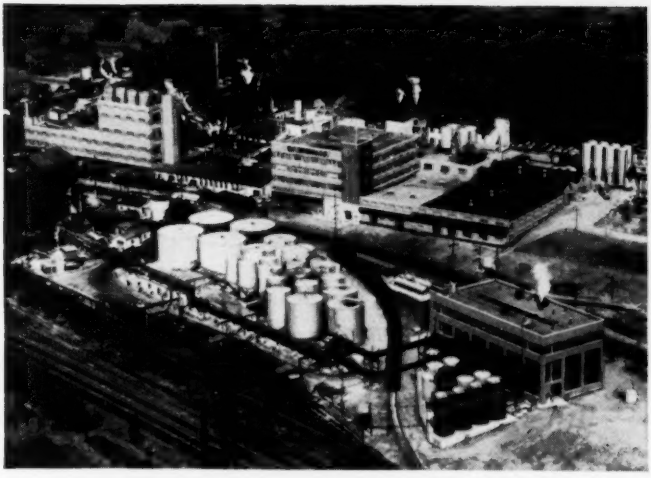

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